

2. DIESEL EMISSIONS CHARACTERIZATION, ATMOSPHERIC TRANSFORMATION, AND EXPOSURES

2.1. INTRODUCTION

The intent of this chapter is to provide background information relating to the diesel engine, the pollutants it emits, the history of its use in highway vehicles and railroad locomotives, diesel exhaust composition and emissions trends, and air pollution regulatory standards for diesel engines in the United States. The chapter also provides specific information about physical and chemical composition of diesel exhaust, descriptions of its atmospheric transformations, observations of measured and modeled ambient concentrations (considered alone and as a component of atmospheric particles in general), and some preliminary estimates of population exposures. This information provides background information that is used in conjunction with the toxicological and epidemiology data to formulate the conclusions about human health hazards that are discussed in later chapters of this document. The exposure information does not represent a formal or rigorous exposure assessment; it is only intended to provide a context for the health effects data and health hazard findings.

The diesel engine was patented in 1892 by Rudolf Diesel, who conceived it as a prime mover that would provide much improved fuel efficiency compared with spark-ignition engines. To the present day, the diesel engine's excellent fuel economy remains one of its strongest selling points. In the United States, the diesel engine is used mainly in trucks, buses, agricultural and other off-road equipment, locomotives, and ships.

The chief advantages of the diesel engine over the gasoline engine are its fuel economy and durability. Diesel engines, however, emit a higher mass of carbonaceous particulate matter than do gasoline engines. Over the past decade, modifications of diesel engine components have substantially reduced particle emissions (Hammerle et al., 1994; Sawyer and Johnson, 1995).

The diesel engine compresses air to high pressure and temperature. Fuel, when injected into this compressed air, autoignites, releasing its chemical energy. The resulting combustion gases expand, doing work on the piston, before being exhausted to the atmosphere. Power output is controlled by the amount of injected fuel rather than by throttling the air intake. Compared to its spark-ignited (SI) counterpart, the diesel engine's superior efficiency derives from a higher compression ratio and no part-load throttling. To ensure structural integrity for prolonged reliable operation at the higher peak pressures brought about by a higher compression ratio and autoignition, the structure of a diesel engine generally is more massive than its SI counterpart.

Diesel engines (also called compression-ignition, CI) may be broadly identified as being either two- or four-stroke cycle, injected directly or indirectly, and naturally aspirated or

supercharged. They also are classified according to service requirements such as light-duty (LD) or heavy-duty (HD) automotive/truck, small or large industrial, and rail or marine.

All diesel engines use hydraulic fuel injection in one form or another. The fuel system must meet four main objectives if a diesel engine is to function properly over its entire operating range. It must: (1) meter the correct quantity of fuel, (2) distribute the metered fuel to the correct cylinder, (3) inject the metered fuel at the correct time, and (4) inject the fuel so that it is atomized and mixes well with the in-cylinder air. The first two objectives are functions of a well-designed injection pump, and the last two are mostly functions of the injection nozzle. As a part of the effort to obtain lower exhaust emissions without diminishing fuel efficiency, fuel injection systems are moving toward the use of electronic components for more flexible control than is available with purely mechanical systems.

Both the fuel and the lubricants that are used to service diesel engines are highly finished petroleum-based products combined with chemical additives. Diesel fuel is a mixture of many different hydrocarbon molecules from about C₇, to about C₃₅, with a boiling range from roughly 350 to 650°F. Many of the fuel and oil properties, such as its specific energy content (which is higher than gasoline), ignition quality, and specific gravity, are related to its hydrocarbon composition. Therefore, fuel and lubricant composition affects many aspects of engine performance, including fuel economy and exhaust emissions.

Complete and incomplete combustion of fuel in the diesel engine results in the formation of a complex mixture of gaseous and particulate exhaust. Because of concerns over health effects associated with diesel particulate emissions, EPA began regulating emissions from diesel engines in 1970 (for smoke) and then added regulations for gaseous emissions. EPA first regulated particulate emissions from HD diesels in 1988.

This chapter begins with background information regarding the formation of primary emissions resulting from diesel combustion, a summary of EPA emission standards for on-road and locomotive diesel engines, and a description of the national trends in emissions from on- and off-road diesel sources. The chapter continues with a description of engine technologies and the history of dieselization for on-road vehicles and locomotives, then provides a chronological assessment of emission rates and the chemical and physical nature of emissions. The data describing diesel engine emissions consider primary emissions, which undergo chemical and physical transformations in the atmosphere. Since the atmospheric transformations potentially have important impacts on environmental and human health, the available information regarding these transformations is discussed. This chapter concludes with a summary of the available literature regarding concentrations and exposures to diesel particulate matter (PM) in different exposure settings.

2.2. PRIMARY DIESEL EMISSIONS

2.2.1. Diesel Combustion and Formation of Primary Emissions

A basic understanding of diesel combustion processes can assist in understanding the complex factors that influence the formation of PM and other diesel exhaust emissions. Unlike spark-ignition combustion, diesel combustion is a fairly nonhomogenous process. Fuel is sprayed at high pressure into the compressed cylinder contents (primarily air with some residual combustion products) as the piston nears the top of the compression stroke. The turbulent mixing of fuel and air that takes place is enhanced by injection pressure, the orientation of the intake ports (e.g., inducement of intake-swirl tangential to the cylinder wall), piston motion, and piston bowl shape. In some cases fuel and air mixing is induced via injection of the fuel into a turbulence-generating pre-chamber or swirl chamber located adjacent to the main chamber (primarily in older, higher speed engines and some LD diesels). Examples of typical direct injection (DI) and indirect injection (IDI) combustion systems are compared in Figure 2-1. Diesel combustion can be considered to consist of the following phases (Heywood, 1988; Watson and Janota, 1982):

1. An ignition delay period, which starts after the initial injection of fuel and continues until the initiation of combustion. The delay period is governed by the rate of fuel and air mixing, diffusion, turbulence, heat transfer, chemical kinetics, and fuel vaporization. Fuel cetane rating is an indication of ignition delay.
2. Rapid, premixed burning of the fuel and air mixture from the ignition delay period.
3. Diffusion-controlled burning, in which the fuel burns as it is injected and diffuses into the cylinder.
4. A very small amount of rate-controlled burning during the expansion stroke, after the end of injection.

Engine speed and load are controlled by the quantity of fuel injected. Thus, the overall fuel-to-air ratio varies as engine speed and load vary. On a macro scale the cylinder contents are always fuel-lean. Depending on the time available for combustion and the proximity of oxygen, the fuel droplets are either completely or partially oxidized. At temperatures above 1300 K, unburned fuel that is not oxidized is pyrolyzed (stripped of hydrogen) to form elemental carbon soot (Dec and Espey, 1995). Soot formation occurs primarily during the diffusion-burn phase of combustion, and is highest during high load and other conditions consistent with high fuel-air

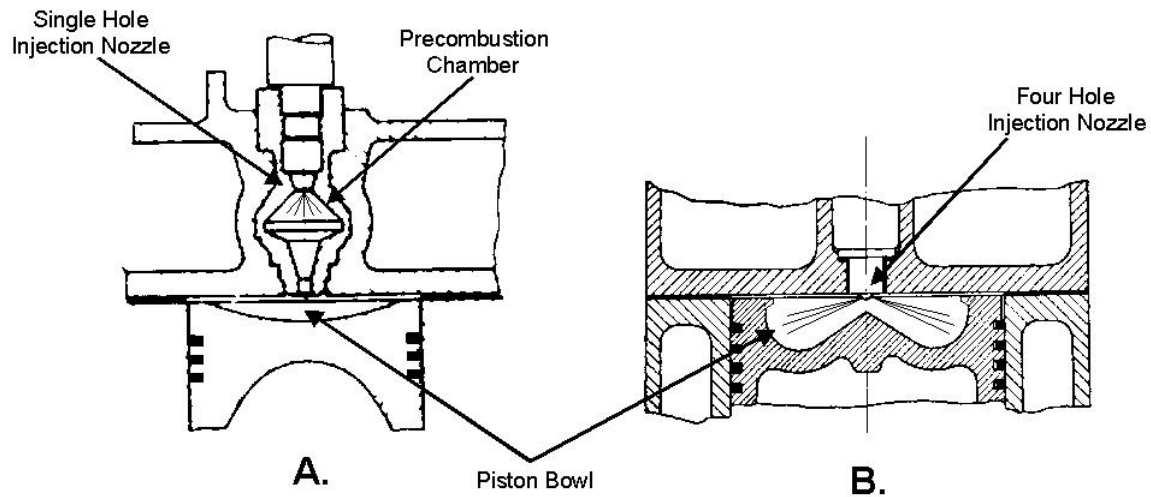


Figure 2-1. A comparison of IDI (A) and DI (B) combustion systems of high-speed, HD diesel truck engines. DI engines almost completely replaced IDI engines for these applications by the early 1980s.

1 equivalence ratios. Most of the soot formed (80% to 98%) is oxidized during later stages of
 2 combustion, most likely by hydroxyl (OH) radicals formed during combustion (Kittelson et al.,
 3 1986; Foster and Tree, 1994). The remainder of the soot leaves as a component of PM emissions
 4 from the engine.

5 During combustion, sulfur compounds present in the fuel are oxidized to sulfur dioxide
 6 (SO_2). Approximately 1% to 4% of fuel sulfur is oxidized to SO_3 , which combines with water
 7 vapor in the exhaust to form sulfuric acid (H_2SO_4) (Wall et al., 1987; Khatri et al., 1978;
 8 Baranescu, 1988). Upon cooling, sulfuric acid and water condense into an aerosol that is
 9 nonvolatile under ambient conditions. The mass of sulfuric acid PM is more than doubled by the

mass of water associated with the sulfuric under typical PM measurement conditions (50% relative humidity, 20-25 °C) (Wall et al., 1987).

Oxide of nitrogen (NO_x) emissions from combustion engines, primarily (at least initially) in the form of NO, are generally thought to be formed via the Zeldovich mechanism, which is highly temperature dependent. High combustion temperatures cause reactions between oxygen and nitrogen to form NO and some NO_2 . The majority of NO_2 formed during combustion is rapidly decomposed. NO can also decompose to N_2 and O_2 , but the rate of decomposition is very slow because of the rapidly decreasing temperatures from the expansion of combustion gases during the expansion stroke (Heywood, 1988; Watson and Janota, 1982). Thus, most of the NO_x emitted is NO.

Some organic compounds from unburned fuel and from lubricating oil consumed by the engine can be trapped in crevices or cool spots within the cylinder and thus are not sufficiently available to conditions that would lead to their oxidation or pyrolysis. These compounds are emitted from the engine and either contribute to gas-phase organic emissions or to PM emissions, depending on their volatility. Within the exhaust system, temperatures are sufficiently high that these compounds are entirely present within the gas phase (Johnson and Kittelson, 1996). Upon cooling and mixing with ambient air in the exhaust plume, some of the less volatile organic compounds can adsorb to the surfaces of soot particles. Lacking sufficient soot adsorption sites, the organic compounds may condense on sulfuric acid nuclei (Abdul-Khalek et al., 1999).

Metallic compounds from engine component wear, and from compounds in the fuel and lubricant, contribute to PM mass. Ash from oil combustion also contributes trace amounts to PM mass.

2.2.2. Diesel Emission Standards and Emission Trends Inventory

EPA set a smoke standard for on-road HD diesel engines beginning with the 1970 model year, and then added a CO standard and a combined hydrocarbon (HC) and NO_x standard for the 1974 model year, as detailed in Table 2-1. Beginning in the 1979 model year, the EPA added a HC standard while retaining the combined HC and NO_x standard. All of the testing for HC, CO, and NO_x was completed using a steady state test procedure. Beginning in the 1985 model year, the EPA added a NO_x standard, dropped the combined HC and NO_x standard, and converted from steady-state to transient testing for HC, CO, and NO_x emissions. EPA introduced a particulate standard for the 1988 model year.

Since the 1985 model year, only the NO_x and particulate standards have been tightened for diesel engines. For truck and bus engines, the particulate standard was reduced in 1991, and again in 1994 for truck engines. For urban bus engines, the particulate standard was reduced in

Table 2-1. Emission standards: HD highway diesel engines

Model year	Pollutant (g/bhp-hr)					Smoke ^a
	HC	CO	NO _x	HC + NO _x	Particulate (PM) t=truck, b=bus, ub=urban bus	
1970	----	-----	-----	-----	----	A:40%; L:20%
1974	----	40	-----	16 ^b	----	A:20%; L:15%; P:50%
1979	1.5	25	-----	10 ^b	----	A:20%; L:15%; P:50%
1985 ^c	1.3	15.5	10.7	----	----	A:20%; L:15%; P:50%
1988	1.3	15.5	10.7	----	0.60	A:20%; L:15%; P:50%
1990	1.3	15.5	6.0	----	0.60	A:20%; L:15%; P:50%
1991	1.3	15.5	5.0	----	0.25	A:20%; L:15%; P:50%
1993	1.3	15.5	5.0	----	0.25 t, 0.10 b	A:20%; L:15%; P:50%
1994	1.3	15.5	5.0	----	0.10 t, 0.07 ub	A:20%; L:15%; P:50%
1996	1.3	15.5	5.0	----	0.10 t, 0.05 ub	A:20%; L:15%; P:50%
1998	1.3	15.5	4.0	----	0.10 t, 0.05 ub	A:20%; L:15%; P:50%
2004	1.3	15.5	----	2.4 NMHC ^d	0.10 t, 0.05 ub	A:20%; L:15%; P:50%

^aEmissions measured in percent opacity during different operating modes: A=Acceleration; L=Lug; P=Peaks during either mode.

^bTotal HC.

^cIn 1985, test cycle changed from steady-state to transient operation for HC, CO, and NO_x, measurement and in 1988 for PM.

^dOr 2.5 plus a limit of 0.5 nonmethane hydrocarbon (NMHC).

1994 and again in 1996. The NO_x standard was reduced in 1998 for all on-road diesel engines, bus and truck. For 2004, the standards were further lowered in a 1997 rulemaking, with limits on non-methane hydrocarbon (NMHC) and NO_x combined, but no further reductions in CO, particulate matter, or smoke. These lower NMHC-plus-NO_x levels will very likely be confirmed in the “1999 technology review” of these standards. EPA is currently evaluating further reductions in NO_x and particulate matter for the post-2004 time frame.

In December 1997, the EPA adopted emission standards for NO_x, HC, CO, PM, and smoke for newly manufactured and remanufactured railroad locomotives and locomotive engines. The rulemaking, which takes effect in the year 2000, applies to locomotives originally manufactured from 1973, any time they are manufactured or remanufactured (locomotives originally manufactured before 1973 are not regulated). Three sets of emission standards have been manufactured from 1973 through 2001 (Tier 0), from 2002 through 2004 (Tier 1), and in 2005 and later (Tier 2) (Table 2-2; see EPA web page at <http://www.epa.gov/omswww/or>

<http://www.dieselnet.com/standards/> for current information on mobile source emission standards). The emissions are measured over two steady-state test cycles which represent two different types of service, including the line-haul (long-distance transport) and switch (involved in all transfer and switching operations in switch yards) locomotives.

The EPA emission trends report (U.S. EPA, 1998a) provides emission inventories for criteria pollutants (PM₁₀, PM_{2.5}, SO₂, NO_x, VOC, CO, Pb, and NH₃) from point, area, and mobile sources, which indicate how emissions have changed from 1970 to 1977. For the purposes of this document, primary and secondary emissions from diesel engines (on- and off-road) are briefly discussed for PM₁₀, sulfur dioxide (SO₂), nitrogen oxides (NO_x), and volatile organic compounds (VOC).

Mobile-source particulate emissions come from both gasoline- and diesel-powered engines in on-road vehicles and from a number of nonroad sources. Nonroad sources include aircraft, commercial boats (which are mainly diesel-powered), construction equipment, agricultural equipment, lawn/garden equipment, and other sources. The EPA emission trends report shows that among point, area, and mobile sources (excluding fugitive dust sources), mobile sources are responsible for 24% of PM₁₀ emissions, with stationary sources (fuel combustion and industrial processes) responsible for the remainder.

Particulate emissions from diesels are much greater than those from gasoline-fueled engines. Particulate emissions (PM₁₀) from gasoline-fueled engines decreased dramatically in 1975 with the widespread introduction of unleaded gasoline. Particulate emissions from diesel highway vehicles have decreased recently because of EPA emission standards for new model

Table 2-2. Emission standards: locomotives (g/bhp/hr)

	Year ^a	CO	HC	NO _x	PM
Line-haul	1973-2001 (Tier 0)	5.0	1.0	9.5	0.6
Switch	1973-2001 (Tier 0)	8.0	2.1	14.0	0.72
Line-haul	2002-2004 (Tier 1)	2.2	0.55	7.4	0.45
Switch	2002-2004 (Tier 1)	2.5	1.2	11.0	0.54
Line-haul	2005 + (Tier 2)	1.5	0.3	5.5	0.20
Switch	2005 + (Tier 2)	2.4	0.6	8.1	0.24

^aDate of engine manufacture.

year HD diesel trucks that were first implemented in 1988 and became increasingly stringent in 1991 and 1994, as presented in Table 2-1 above.

The EPA emission trends report indicates that annual on-road vehicle PM₁₀ emissions decreased from 397,000 tons to 268,000 tons from 1980 to 1997. Passenger car particulate emissions decreased from 120,000 to 56,000 tons (53%) in this time frame while diesel vehicle emissions decreased much less, from 208,000 to 163,000 tons (22%). Nonroad diesel engine particulate emissions decreased from 439,000 tons in 1980 to 316,000 tons in 1997 (28%). Emissions data for PM_{2.5} are available only for the period from 1990 to 1997, prohibiting an analysis of emission trends over the same time period as the other pollutants. For comparison to PM₁₀, annual on-road diesel vehicle PM_{2.5} emissions were estimated at 144,000 tons in 1997 and nonroad diesel PM_{2.5} emissions in 1997 were 290,000 tons.

Diesel engines also contribute to secondary PM formation from NO_x and SO₂ emissions that are converted to nitrate and sulfate, although the direct emission of carbonaceous diesel particulates are much greater than secondary nitrate or sulfate formation. In 1997, about 50% of total ambient NO_x came from mobile sources, with diesels responsible for 26%, or approximately half of the mobile source contribution. About 6% of SO₂ came from mobile sources in 1997, with diesels responsible for 80% of that total. VOC emissions from diesel engines in 1997 were estimated at 4% of the total emissions from all sources.

2.2.3. Engine Technology Description and Chronology

NO_x emissions, PM emissions, and brake-specific fuel consumption (BSFC) are among the parameters that are typically considered during the development of a diesel engine. Many engine variables that decrease NO_x can also increase PM and BSFC. One manifestation of the interplay among NO_x, PM, and BSFC is that an increase in combustion temperatures will tend to increase NO formation via the Zeldovich mechanism, will often improve thermal efficiency, can improve BSFC, and can increase the rate of PM oxidation, thus lowering PM emissions. One example of this is the tradeoff of PM emissions and BSFC versus NO_x emissions with fuel injection timing. Many recent advances in reducing the engine-out emissions of diesel engines are combinations of technologies that provide incremental improvements in the tradeoffs among these different emissions and fuel consumption. The sum total, though, can be considerable reductions in regulated emissions within acceptable levels of fuel consumption.

The majority of current HD diesel truck engines certified for use in the United States utilize:

- a 4-stroke cycle;

- direct-injection, high-pressure (1200 bar to >2000 bar) fuel injection systems with electronic control of injection timing and, in some cases, injection rate;
- centrally located multihole injection nozzles;
- 3 or 4 valves per cylinder;
- turbochargers;
- in many cases, air-to-air aftercooling; and
- in some cases, the use of an oxidation catalyst.

These features have phased into use with HD truck engines because they offer a relatively good combination of fuel consumption, torque-rise, emissions, durability, and the ability to better “tune” the engines for specific types of applications. Fuel consumption, torque-rise, and drivability have been maintained or improved while emissions regulations have become more stringent. Many Class 8a and 8b diesel truck engines are now capable of 700,000 to 1,000,000 miles of driving before their first rebuild, and can be rebuilt several times because of their heavy construction and the use of removable cylinder liners. This is several times the regulatory estimate of full useful life for HD engines (290,000 miles) previously used by EPA.

Current 4-stroke locomotive engines use engine technology similar to on-highway diesel engines, except that electronic controls have only recently been introduced. It is difficult to separate the components of current high-speed diesel engines for discussion of their individual emissions effects. Most of the components interact in numerous ways that affect emissions, performance, and fuel consumption.

2.2.3.1. Injection Rate

Decreasing the duration of diffusion combustion and promoting soot oxidation during the expansion stroke can reduce formation of soot agglomerates (Stone, 1995). Both of these effects are enhanced by increasing the fuel injection rate. The primary means of accomplishing this is by increasing fuel injection pressure. Increased injection rate can significantly reduce soot emissions, but it can also increase combustion temperatures and cause an increase in NO_x emissions (Springer, 1979; Watson and Janota, 1982; Stone, 1995). However, when combined with turbocharging, aftercooling, and injection timing retard, low NO_x, low PM, and relatively good BSFC and brake mean engine pressure (BMEP) are possible.

In 1977 Robert Bosch introduced a new type of high-pressure pump capable of producing injection pressures of 1700 bar at the nozzle (Voss et al., 1977). This increased fuel injection pressure by roughly a factor of 10. Unit injection, which combines each fuel injection nozzle with individual cam-driven fuel pumps, can achieve very high injection pressures (>2000 bar). The first combination of unit injectors with electronically controlled solenoids for timing control was

1 offered in the United States by Detroit Diesel Corporation in the 1988 model year (Hames et al.,
2 1985). Replacement of the injection cam with hydraulic pressure, allowing a degree of injection
3 rate control, was made possible with the hydraulic-electronic unit injection (HEUI) jointly
4 developed by Caterpillar and Navistar, introduced on the Navistar T444E engine (and variants) in
5 1993.

6 It is widely known that high fuel injection pressures have been used to obtain compliance
7 with the PM standards that went into effect in 1988 (Zelenka et al., 1990). Thus, it is likely that a
8 transition to this technology began in the 1980s, with the vast majority of new engine sales
9 employing this technology by 1991, when the 0.25 g/bhp-h Federal PM standard went into effect.

10 The use of electronic control of injection rate is rapidly increasing on medium-HD diesel
11 engines equipped with HEUI (currently available on Caterpillar 3126 and Navistar T444E,
12 DT466, and 530E engines). Engines are currently under development, perhaps for 2002-2004
13 introduction, that use common-rail fuel injection systems with even more flexible control over
14 injection pressure and timing than previous systems.

15 16 **2.2.3.2. Turbocharging, Charge-Air Cooling, and Electronic Controls**

17 Use of exhaust-driven turbochargers to increase intake manifold pressure has been applied
18 to both IDI and DI diesel engines for more than 40 years. Turbocharging can decrease fuel
19 consumption compared to a naturally aspirated engine of the same power output. Turbocharging
20 utilizes otherwise wasted exhaust heat to generate intake boost. The boosted intake pressure
21 effectively increases air displacement and increases the amount of fuel that can be injected to
22 achieve a given fuel-air equivalence ratio. Turbocharging increases the power density of an
23 engine. Boosting intake pressure via turbocharging and reducing fuel-to-air ratio at a constant
24 power can significantly increase both intake temperatures and NO_x emissions. Increased boost
25 pressure can significantly reduce ignition delay, which reduces VOC and PM soluble organic
26 fraction (SOF) emissions (Stone, 1995) and increases the flexibility in selection of injection
27 timing. Injection timing on turbocharged engines can be retarded further for NO_x emission
28 control with less of an effect on PM emissions and fuel consumption. This allows a rough parity in
29 NO_x emissions between turbocharged (non-aftercooled) and naturally aspirated diesel engines
30 (Watson and Janota, 1982).

31 Turbocharging permits the use of higher initial injection rates (higher injection pressure),
32 which can reduce particulate emissions. Although this may offer advantages for steady-state
33 operation, hard accelerations can temporarily cause overly fuel-rich conditions because the
34 turbocharger speed lags behind a rapid change in engine speed (turbo-lag). This can cause
35 significant increases in PM emissions during accelerations. Before the advent of electronic
36 controls, the effect of acceleration on PM emissions could be limited by mechanically delaying

demand for maximum fuel rate with a “smoke-puff eliminator.” Since this device also limited engine response, there was considerable incentive for the end-users to remove or otherwise render the device inactive. Charge-air cooling, for example using an air-to-air aftercooler (air-cooled heat exchanger) between the turbocharger compressor and the intake manifold, can greatly reduce intake air and peak combustion temperatures. When combined with injection timing retard, charge-air cooling allows a significant reduction in NO_x emissions with acceptable BSFC and PM emissions when compared to either non-aftercooled or naturally aspirated diesel engines (Hardenberg and Fraenkle, 1978; Pischinger and Cartellieri, 1972; Stone, 1995) (Figure 2-2).

Electronic control of fuel injection timing allowed engine manufacturers to carefully tailor the start and length of the fuel injection events much more precisely than through mechanical means. Because of this, newer on-highway turbocharged truck engines have virtually no visible smoke on acceleration. Electronic controls also allowed fuel injection retard under desirable conditions for NO_x reduction, while still allowing timing optimization for reduced VOC emissions on start-up, acceptable cold-weather performance, and acceptable performance and durability at high altitudes. Previous mechanical unit injected engines (e.g., the 1980s Cummins L10, the non-DDEC DDC 6V92) were capable of reasonably high injection

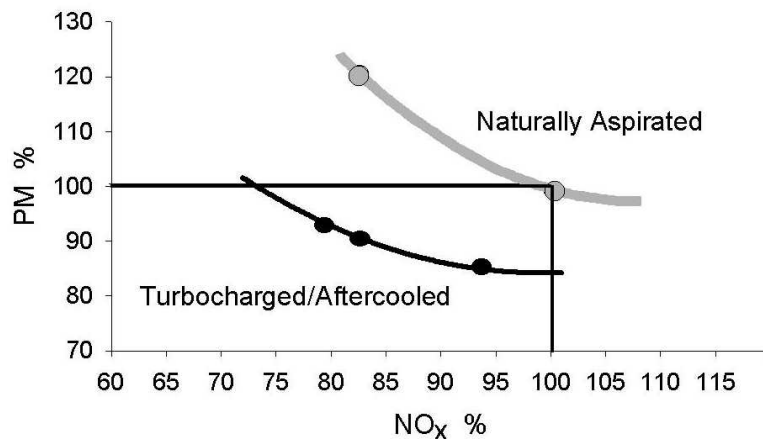


Figure 2-2. Effect of turbocharging and aftercooling on NO_x and PM (Mori, 1997).

pressures, but had fixed injection timing that only varied based on the hydraulic parameters of the fuel system. Many other engines with mechanical in-line or rotary injection pumps had only coarse injection timing control or fixed injection timing.

Precise electronic control of injection timing over differing operating conditions also allowed HD engine manufacturers to retard injection timing for low NO_x emissions during highly

transient urban operation similar to that found during emissions certification, and advance the injection timing during less transient operation (such as freeway driving) for fuel consumption improvements (~3% to 5%) at the expense of greatly increased NO_x emissions (~3 to 4 times regulated levels). This particular situation resulted in the recent consent-decree settlements between the Federal Government and most of the HD engine manufacturers to assure effective NO_x control in all driving conditions.

Turbocharged engines entered the market very slowly beginning in the 1960s. During the years 1949 to 1975 the total improvement in emissions for the on-road diesel fleet was considerably less than 10%-20% for gaseous emissions and, for particulates, there was really no change at all until the advent of particulate standards in 1988. Charge air cooling was introduced during the 1960s and was initially performed in a heat exchanger using engine coolant. Cooling of the charge air using ambient air as the coolant was introduced by Mack in 1977 with production of the ETAY(B)673A engine (Heywood, 1988). Use of ambient air allowed cooling of the charge air to much lower temperatures. Most HD diesel engines sold today employ some form of charge air cooling, with air-to-air aftercooling the most common. Johnson and co-workers (Johnson et al., 1994) have presented a comparison of similar engines that differ in that the charge air is cooled by engine coolant (1988 engine) and by ambient air with a higher boost pressure for the second (1991 engine). The 1991 engine also used higher pressure fuel injectors. The 1991 engine exhibited both lower PM (50%) and NO_x emissions. Higher injection pressure likely enabled the reduced PM emissions, while the lower charge air temperature and the ability to electronically retard the injection timing under some conditions likely enabled the lower NO_x emissions.

It is apparent on the basis of both the literature and certification data that turbochargers with aftercoolers can be used in HD engines in conjunction with other changes to result in a decrease in emissions. NO_x was probably reduced on the order of 10% to 30% in turbocharged aftercooled engines with retarded injection timing. Prior to the late 1970s, only a portion of all HD diesel engines were turbocharged, so the total improvement in emissions that could be associated with these changes was considerably less until more stringent emissions regulations were implemented. The lowest combination of in-use NO_x and PM emissions would likely be for turbocharged aftercooled engines that used retarded, high-pressure unit injection without electronic control in the early 1990s. Although tighter NO_x standards phased in for model years 1994 and 1998, this is complicated by the instances of defeating NO_x control during cruise conditions by most engine manufacturers. Defeat of NO_x control occurred to a different extent with all Class 8 electronically controlled engines beginning with their introduction in 1988. PM emissions were likely much lower for engines on which electronic controls were introduced, but NO_x emissions in-use were likely much higher than for early electronic or late mechanically

1 injected versions of the engines. Overall, it is expected that engines in the 1950 to 1980 time
2 frame would have PM emissions similar to those of the mid-1980 engines that were not yet
3 controlled for particulates, while later engines would have lower PM emissions.
4

5 **2.2.3.3. Indirect and Direct Injection High-Speed Diesel Engines**

6 Prior to the 1930s, diesel engine design was limited to relatively low-speed applications
7 because sufficiently high-pressure fuel injection equipment was not available. With the advent of
8 high-speed and higher pressure pump-line-nozzle systems, introduced by Robert Bosch in the
9 1930s, it became possible to inject the fuel directly into the cylinder for the first time, although
10 IDI diesel engines continued in use for many years. As diesels were introduced into the heavy
11 truck fleet in the 1930s through the 1950s, both IDI and DI naturally aspirated variants were
12 evident. A very low-cost, rotary injection pump technology was introduced by Roosa-Master in
13 the 1950s, reducing the cost of DI systems and allowing their introduction on smaller
14 displacement, higher speed truck engines.

15 DI diesel engines have now all but replaced IDI diesel engines for HD on-highway
16 applications¹. IDI engines typically required much more complicated cylinder head designs, but
17 generally were capable of using less sophisticated, lower pressure injection systems with less
18 expensive single-hole injection nozzles. IDI combustion systems are also more tolerant of lower
19 grades of diesel fuel. Fuel injection systems are likely the single most expensive component of
20 many diesel engines. Caterpillar continued producing both turbocharged and naturally aspirated
21 IDI diesel engines for some on-highway applications into the 1980s. Caterpillar and Deutz still
22 produce engines of this type, primarily for use in underground mining applications. IDI
23 combustion systems are still used in many small-displacement (<0.5 L/cylinder), very high-speed
24 (>3000 rpm rated speed) diesel engines for small offroad equipment (small imported tractors,
25 skid-steer loaders), auxiliary engines, and small generator sets.

26 IDI engines have practically no premixed burn combustion, and thus are often quieter and
27 have somewhat lower NO_x emissions than DI engines. Electronic controls, high-pressure
28 injection (e.g., GM 6.5), and 4-valve/cylinder designs (e.g., the 6-cylinder Daimler LD engine) can
29 be equally applied to IDI diesel engines as with their DI counterparts, but negate any advantages
30 in cost over DI engines. DI diesel engines of the same power output consume 15%-20% less fuel
31 than IDI engines (Heywood, 1988). Considering the sensitivity of the HD truck market to fuel
32 costs, this factor alone likely accounts for the demise of IDI diesel engines in these types of

¹The GM Powertrain/AM General 6.5L electronically controlled, turbocharged IDI-swirlchamber engine, certified as a light-HD diesel truck engine, is the last remaining HD on-highway IDI engine sold in the United States.

1 applications. Throttling and convective heat transfer through the chamber-connecting orifice, and
2 heat rejection from the increased surface area of IDI combustion systems, decreases their
3 efficiency and can cause cold-start difficulties when compared to DI designs. Most IDI diesel
4 engine designs require considerably higher than optimum (from an efficiency standpoint)
5 compression ratios to aid in cold starting (19:1 to 21:1 versus ~15:1 to 17:1 for DI engines).

6 Because of the early introduction of DI technology into truck fleets, it is likely that by end
7 of the 1970s, only a small fraction of the HD diesel engines sold for on-highway use were IDI
8 engines. It is unlikely that the gradual shift from IDI to DI engine designs through the 1960s and
9 1970s had any significant impact on emissions.

10 11 **2.2.3.4. Two-Stroke and 4-Stroke High-Speed Diesel Engines**

12 A detailed discussion of the 2- and 4-stroke engine cycles can be found in Heywood,
13 Taylor, or Stone, and so will not be presented here (Heywood, 1988; Taylor, 1990; Stone, 1995).
14 Nearly all high-speed 2-stroke diesel engines utilize uniflow scavenging assisted by a positive
15 displacement blower (Figure 2-3). Uniflow-scavenged 2-stroke diesels use poppet exhaust valves
16 similar to those found in 4-stroke engines. The intake air enters the cylinder through a
17 pressurized port in the cylinder wall. A crankshaft-driven, positive-displacement blower (usually a
18 roots-type) pressurizes the intake port to ensure proper scavenging. A turbocharger may be added
19 to the system to provide additional boost upstream of the blower at higher speeds, and to reduce
20 the size and parasitic losses associated with the positive-displacement blower.

21 Two-stroke diesel engines can achieve efficiency comparable to 4-stroke counterparts and
22 have higher BMEP (torque per unit displacement) (Heywood, 1988). It is useful to note that the
23 2-stroke cycle fires each cylinder once every revolution, while the 4-stroke cycle fires every other
24 revolution. Thus, for a given engine size and weight, 2-strokes can produce more power.
25 However, 2-stroke diesel engines are less durable than their 4-stroke counterparts. Lubricating
26 oil is transferred from the piston rings to the intake port, which causes relatively high oil

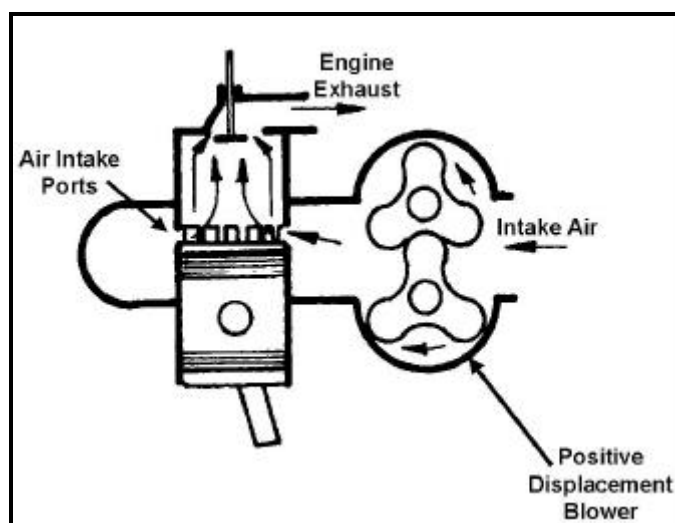


Figure 2-3. An example of uniflow scavenging of a 2-stroke diesel engine with a positive displacement blower (Adapted from Taylor, 1990). Scavenging is the process of simultaneously emptying the cylinder of exhaust and refilling with fresh air.

consumption relative to 2-stroke designs. Durability and low oil consumption are desirable for on-highway truck applications. This may be why 4-stroke engines have been favored for these applications since the beginning of dieselization in the trucking industry, with the notable exception of urban bus applications. Although it is no longer in production, the Detroit Diesel 6V92 series of 2-stroke diesel engines is still the most popular for urban bus applications, where the high power density allows the engine to be more easily packaged within space limitations. The primary reason that 2-stroke engines like the 6V92 are no longer offered for urban bus applications is PM emissions. The reduced lubricating oil control with 2-strokes tends to increase VOC and organic PM emissions relative to 4-stroke designs. This was particularly problematic for urban bus applications because urban bus engines must meet tighter Federal and California PM emissions standards. The current urban bus PM standard (0.05 g/bhp-hr) is half of the current on-highway HD diesel engine PM standard. No 2-stroke diesel engine designs have been certified to meet the most recent urban bus PM emissions standards, and Detroit Diesel Corporation has not certified a 2-stroke diesel engine for on-highway truck use since 1995.

A comprehensive review of emissions from hundreds of later model vehicles (1976-1998) found no significant difference between 2- and 4-stroke vehicles (Yanowitz et al., 1999a). Overall, regulated emissions changes due to changing proportions of 2- and 4-stroke engines in the in-use fleet during the years 1949-1975 do not appear to be significant for HD truck and bus

engines. Furthermore, it appears that the proportion of 2-stroke engines in the in-use fleet was relatively constant until the 1980s.

2.2.3.5. Near-Term Diesel Emission Reduction Technologies

2.2.3.5.1. Exhaust gas recirculation. Exhaust gas recirculation (EGR) (i.e., routing some of the exhaust gas to the intake manifold) is widely used in LD SI gasoline engines to control NO_x emissions. Unlike most SI applications, use of EGR with diesels necessitates both electronic control of the EGR as well as EGR cooling to limit the associated increase in PM. Because EGR displaces part of the intake air, it can increase the overall fuel-to-air equivalence ratio to a point that can lead to large increases in PM emissions. Hot EGR further exacerbates this problem by increasing the temperature of the intake air. The increased temperature decreases air density and further reduces the volume of intake air entering the engine.

Cooled EGR systems typically use an engine coolant heat exchanger to cool the recirculated exhaust gases before mixing with the intake air. EGR cooling has the potential to significantly reduce the increase in intake air temperature associated with EGR. This would mitigate (though not eliminate) the PM emissions penalty associated with diesel EGR systems. Though EGR cooling greatly extends the operational range over which EGR can be used, electronic control of the EGR will be necessary to prevent large PM increases under hard acceleration, near peak torque conditions, or at high altitudes. EGR cooling can also reduce combustion temperatures beyond uncooled EGR, resulting in further decreases in NO_x emissions relative to uncooled EGR under certain conditions (Kakoi et al., 1998; Leet et al., 1998).

Cooled EGR is currently used with the relatively small number of LD diesel vehicles sold for the U.S. market. Although it is not widely used in HD diesel engines today, many believe that cooled EGR will be an important technology for future NO_x reductions (Johnson et al., 1994; Zelenka, 1990). Most, if not all, of the diesel engines that will meet either the 2002 consent decree requirements (early compliance with 2004 standards) or the 2004 emissions standards for HD trucks will incorporate some form of cooled EGR into their engine designs to meet the 2.5 g/bhp-hr NO_x + NMHC standard.

Ladomatos et al. (1996-1997) have described the three mechanisms by which EGR is thought to lead to reduced emissions of NO_x:

- *Dilution:* Recirculating exhaust gas leads to a reduction in the oxygen content of the intake charge. Although this increases ignition delay, it also reduces peak temperature. With respect to NO formation, the increased ignition delay and premixed burn fraction are more than offset by the dilution effects on peak temperature, resulting in a significant reduction in NO_x emissions. The reduction

1 in oxygen content can also cause an increase in HC, CO, and PM emissions. The
2 dilution mechanism is thought to be, by far, the most important mechanism
3 affecting diesel engine emissions.

- 4 • *Thermal:* The recirculated exhaust gas contains CO₂ and water vapor, which
5 increase the specific heat of the intake charge. This lowers peak temperature and
6 hence formation of NO_x is decreased.
- 7 • *Chemical:* It is possible that endothermic dissociation of recirculated CO₂ and
8 water lowers peak temperature, leading to a reduction in formation of NO_x.

9
10 Early studies of uncooled diesel EGR were conducted by Pischinger and Cartellier (1972)
11 and Springer (1979). Although sub-4 g/bhp-hr NO_x emissions levels were possible, the high PM
12 emissions associated with the NO_x reductions delayed the introduction of EGR until fuel sulfur
13 levels were low enough to enable engine-coolant cooling of EGR. Theoretically, further cooling
14 of the EGR (for example, air cooling) would extend the range of engine operating conditions
15 under which EGR could be used, but is not possible at current fuel sulfur levels because of the
16 potential for very high levels of sulfuric acid condensation in the EGR cooler (McKinley, 1997;
17 Kreso et al., 1998a; Leet et al., 1998).

18 Johnson (1994) noted that engine durability is a serious concern with EGR because
19 recirculation of soot through the engine can increase wear. Kreso and co-workers (Kreso et al.,
20 1998b) recently examined a 1995 Cummins M-11 at two steady-state modes and two EGR rates.
21 The EGR system included cooling of the recirculated gas. EGR was effective at reducing NO_x,
22 and reductions as high as 56% were observed under some conditions. Emissions of PM increased
23 by as much as 57%, while emissions of the SOF portion of PM were somewhat lower.
24 Examination of the mutagenicity of SOF with the Ames assay indicated that the SOF produced by
25 EGR was more mutagenic.

26 It is clear that any EGR system will require careful control so that EGR is applied only
27 under operating conditions where significant NO_x reductions can be obtained without a major
28 increase in PM. There is little evidence to suggest that the character of PM, SOF, or gaseous
29 hydrocarbon emissions is dramatically altered by use of EGR.

30
31 **2.2.3.5.2. Diesel oxidation catalysts (DOC).** DOCs for HD diesel applications were originally
32 developed for underground mining equipment for exhaust odor and CO control (typically not
33 issues for diesel engines outside of confined environments). The use of early high-platinum-
34 content DOCs was an issue for these applications because of their high levels of NO to NO₂ and
35 SO₂ to SO₃ oxidation (McClure, 1992). McDonald et al. (1995) found that the SO₃ oxidation rate

was sufficient to produce ~0.2 g/bhp-hr sulfate PM emissions at high load conditions even with a relatively low-sulfur diesel fuel (0.01% S).

Later DOCs were developed that relied more on base metals and less on precious metals for VOC oxidation (lowering SOF PM) while limiting high-temperature formation of sulfuric acid PM. These types of catalysts were first applied to LD diesel vehicles in the 1980s, some urban bus applications (1994 Cummins L10), and a number of medium-HD diesel engines after 1993 (Navistar T444E, some versions of the Caterpillar 3116 and 3126). There are also a number of DOCs that are now being retrofitted to older urban buses as part of the EPA Urban Bus Retrofit and Rebuild Program. Current DOCs oxidize more than 70% of the VOCs that contribute to SOF PM, leading to a 15%-30% reduction in total PM emissions (Farrauto et al., 1996; Brown and Rideout, 1996; Tamanouchi et al., 1998).

DOCs are highly effective at oxidizing lube oil components (Farrauto et al., 1996) as well as most PAHs (Mitchell et al., 1994; Pataky et al., 1994; Bagley et al., 1996; McDonald, 1997; Bagley et al., 1998). There are conflicting data as to whether DOCs catalyze the formation or oxidation of nitro-PAH compounds. Bagley and co-workers (Bagley et al., 1998) and McDonald (1997) found reductions in both PAHs and nitro-PAH and associated mutagenic activity for a low-sulfate-forming base-metal/Pt/Pd oxidation catalyst that were statistically significant at $p < .01$, and found only one nitro-PAH (1-nitropyrene) above minimum detection limits in either catalyzed or uncatalyzed exhaust. Mitchell and co-workers (1994) found decreases in PAHs with twofold increases in nitro-PAH (statistical significance is not known). More comprehensive testing will be necessary to draw further conclusions about the effects of DOCs on nitro-PAH.

2.2.3.6. Future (2004+) Diesel Emission Reduction Technologies

2.2.3.6.1. NO_x storage catalysts. NO_x storage catalysts currently under development might be used to meet 2007 HD diesel engine standards if diesel fuel sulfur levels are considerably reduced (0-30 ppm S fuel may be necessary). A generalized schematic of the operation of this device is included in Figure 2-4. This catalyst system employs a high-platinum (Pt) content catalyst for oxidation of NO to NO_2 (in the absence of an oxidation catalyst, total NO_x in diesel exhaust is primarily NO [typically >90%] with lesser amounts of NO_2). The NO_2 is then stored, using one of a number of barium compounds, as barium nitrate. For approximately 2-second durations every 2 minutes, diesel fuel is either sprayed into the exhaust or injected into the cylinder after combustion to provide the necessary hydrocarbons to remove the NO_x from the storage components. The NO_x is then reduced over a standard three-way catalytic converter.

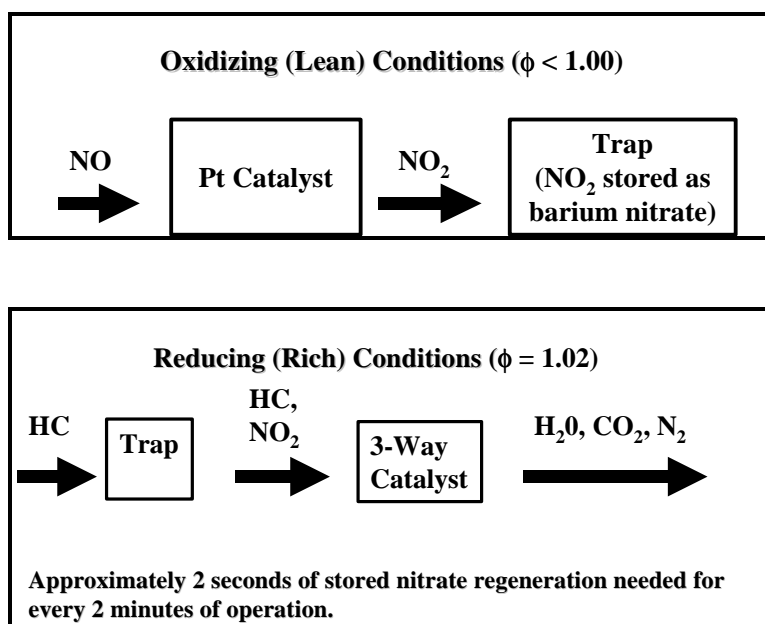


Figure 2-4. NO_x-storage catalyst operation under oxidizing and reducing conditions.

The average NO_x reduction potential for this technology over the FTP is 50% to 75%, with a fuel consumption penalty of approximately 3% to 5% (Wall, 1998). Figure 2-5 compares the NO_x reducing capabilities of a NO_x storage catalyst system to a representative sulfur-tolerant NO_x catalyst system.

2.2.3.6.2. Lean-NO_x catalysts. Various types of active (requiring a post-combustion fuel injection event) and nonactive (no post-injection) lean-NO_x catalysts are in production or are under investigation for continuous reduction of NO_x emissions in lean exhaust environments such as those present in diesel exhaust. (These are continuous devices, as opposed to the cyclic nature of NO_x reduction using NO_x storage catalysts.) Lean-NO_x catalysts typically reduce NO_x efficiently over a very narrow range of exhaust temperatures. There are both high- and low-temperature varieties of lean-NO_x catalysts. Low-temperature, platinum-based lean-NO_x catalysts using zeolites for support, catalyst promotion, and adsorption of NO_x and HC would be typical of a lean-NO_x catalyst technology for medium and light-HD diesel applications. High-temperature base-metal lean-NO_x catalyst formulations (Cu-ZSM, for example) are under investigation primarily for highly loaded HD diesel engine applications.

A number of new common-rail fuel injection systems are capable of injecting fuel after combustion to provide additional hydrocarbons for use as an NO_x reductant with lean-NO_x

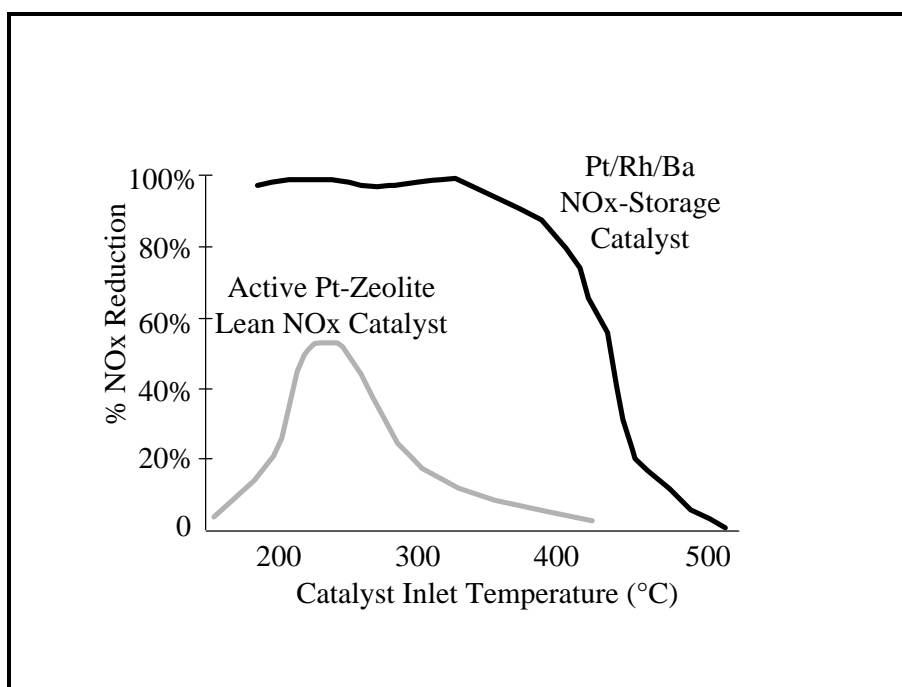


Figure 2-5. A comparison of the NO_x reduction efficiency over a range of temperature conditions for the sulfur-intolerant NO_x storage catalyst system and the more sulfur-tolerant, active Pt-zeolite catalyst system. Although peak NO_x reduction efficiencies for various types of nonstorage lean-NO_x catalysts (similar to the Pt-Zeolite catalyst shown here) approach 50%-60%, average reductions are 15% to 30% over various (FTP-75, NEDC) driving cycles.

1 catalysts. Although active Pt-zeolite catalyst systems have higher NO_x removal efficiencies than
 2 similar nonactive catalyst systems, NO_x removal efficiencies are still only in the range of 15% to
 3 35% over the New European Drive Cycle (NEDC) (Peters et al., 1998; Engler et al., 1998) and
 4 significantly below those of NO_x storage catalyst systems (Figure 2-5). Newer systems use a
 5 controlled fuel-exotherm over the platinum catalysts with feedback control to maintain a more
 6 constant catalyst temperature, enabling higher NO_x reduction efficiencies.

7
 8 **2.2.3.6.3. Selective catalytic reduction.** Selective catalytic reduction (SCR) for NO_x control is
 9 currently available for stationary diesel engines, and has been proposed for mobile light- and
 10 heavy-diesel applications. SCR uses ammonia as a reducing agent for NO_x over a catalyst
 11 composed of precious metals, base metals, and zeolite. The ammonia is supplied by introducing a

urea/water mixture into the exhaust upstream of the catalyst. The urea/water mixture is typically stored in a separate tank that must be periodically replenished. Ammonia has extremely high selectivity as a reductant for NO_x. NO_x reductions of 70% to 90% over a broad range of operating conditions are possible using such systems (Brown, 1998). These systems appear to be tolerant of current U.S. on-highway diesel fuel sulfur levels for exhaust temperatures that are consistent with heavier (Class 7, 8) HD on-highway applications and over the HD FTP test cycle (40 CFR, Subpart N). NO_x reduction efficiency drops considerably at exhaust temperatures less than 200°C in the presence of SO₂ in the exhaust. Therefore, the practical fuel sulfur limit for LD diesel applications is probably somewhat less than 100 ppm. This reduced efficiency at low temperatures and higher fuel sulfur levels may also have implications for “not-to-exceed” NO_x requirements for HD on-highway diesel engines introduced in the consent decrees and likely to be a component of both the 2004 and 2007 HD diesel emissions standards.

Control of the quantity of urea injection into the exhaust, particularly during transient operation, is an important issue with SCR systems. Injection of too large of a quantity of urea leads to a condition of “ammonia slip,” whereby excess ammonia formation can lead to both direct ammonia emissions and oxidation of ammonia to produce (rather than reduce) NO_x. There are also a number of potential hurdles to overcome with respect to using a major emission control system that requires frequent replenishing of a consumable fluid in order to function. This raises issues related to supply, tampering, and the possibility of running the urea storage tank dry. Packaging of the urea supply within the constraints of modern LD vehicles may also be particularly challenging. Packaging of SCR systems does not appear to be a major problem for HD truck or bus applications.

2.2.3.6.4. Continuously regenerating traps. One method of exhaust aftertreatment for controlling diesel PM emissions is to pass diesel exhaust through a ceramic or metallic filter or “PM trap” to collect the PM, and to use some means of burning the collected PM so that the trap can be either periodically or continuously regenerated. Previous traps have used catalyzed coatings, fuel additives, and electrical heating to assist trap regeneration. Failure to consistently regenerate the trap can lead to plugging, excessive exhaust back-pressure, and eventually overheating and permanent damage to the trap. Inconsistent regeneration due to the high frequency of fairly low exhaust temperatures has been a particular problem in applying PM traps to some lightly loaded diesel applications.

The recently developed continuously regenerating trap (CRT) has shown considerable promise in a broad range of diesel applications because of its ability to regenerate even at fairly low exhaust temperatures. The CRT uses nitrogen dioxide (NO₂) to assist trap regeneration. NO₂ can oxidize soot collected within the trap at exhaust temperatures as low as 250°C (Hawker

et al., 1997), which is within the typical exhaust temperature range of many diesel vehicle and truck applications (Lüders et al., 1997). The NO₂ is produced by oxidizing NO in the exhaust using a high-platinum-content oxidation catalyst brick located immediately upstream of the ceramic trap-filter. A general schematic of the CRT system is presented in Figure 2-6.

The CRT is capable of reducing PM emissions by more than 80% (Hawker et al., 1997; Hawker et al., 1998). SO₂ inhibition of NO oxidation effectively limits the CRT to use with diesel fuel sulfur levels below 50 ppm.

In some cases, excess fuel can be used to induce an exotherm over the Pt-catalyst to ensure that minimum soot oxidation temperatures are reached.

It appears likely that introduction of emission standards that would force the use of CRT or similar catalyst/trap technologies would likely be accompanied by steep reductions in toxic emissions. Hawker and co-workers found substantial reductions in gas- and PM-phase VOC, soot, acetaldehyde, formaldehyde, and total particle number (Hawker, 1998). Considering that the CRT incorporates a Pt-DOC, PAHs oxidation is probably also high, but this was not determined in the study.

2.2.3.6.5. Possible effects of advanced aftertreatment systems. *NO₂ formation:* One constant among many of the various proposed diesel exhaust aftertreatment devices is the reliance on high Pt content for some components. In some cases, lean reactions of NO to NO₂ are integral to the

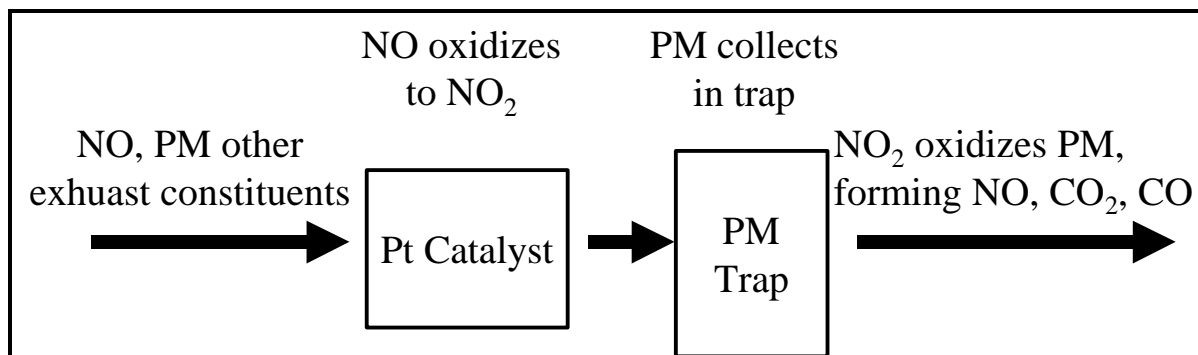


Figure 2-6. Schematic showing the operating principles of the continuously regenerating trap (CRT).

design of the device (CRT, NO_x storage catalyst). In the case of the CRT, >50% conversion of NO to NO₂ is desired for efficient trap regeneration (Figure 2-7). This could result in a significant increase in direct NO₂ emissions from diesel exhaust. In the case of NO_x storage catalysts and SCR, there may be less cause for concern because of the relatively high NO_x reduction efficiencies. Low-temperature lean-NO_x catalysts have relatively high Pt contents, but no data were found in the literature that quantified NO/NO₂ emissions for these devices. *Sulfate*

PM: The relatively high conversion rates of fuel sulfur to sulfuric acid aerosol possible with high-Pt content diesel exhaust aftertreatment systems are similar to those found with early high-Pt DOCs (for example, a Pt lean-NO_x catalyst in Figure 2-8), although it is likely that broad introduction of advanced diesel exhaust aftertreatment systems through reductions in standards for regulated emissions would be accompanied by significant fuel sulfur control.

Ammonia: Widespread use of urea-SCR catalyst systems could increase ammonia emissions. Newer SCR designs are incorporating electronic control of urea injection and the use of a “cleanup” catalyst for oxidation of excess ammonia to minimize ammonia emissions.

PM and VOC: Most of the aftertreatment systems under development are still too new to have been subjected to comprehensive exhaust speciation analyses. The CRT has the additional problem that PM emissions are so low that it is difficult to collect a large enough PM sample for

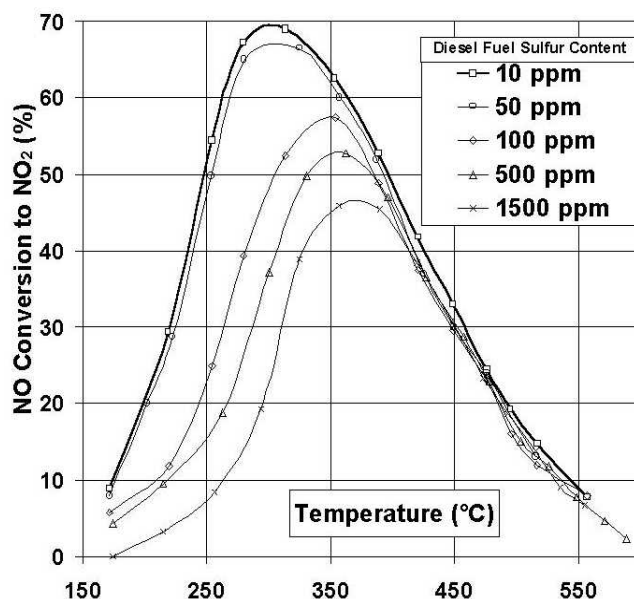


Figure 2-7. Efficiency of NO to NO₂ conversion over the oxidation catalyst component of the CRT at different exhaust temperatures and at differing diesel fuel sulfur levels.

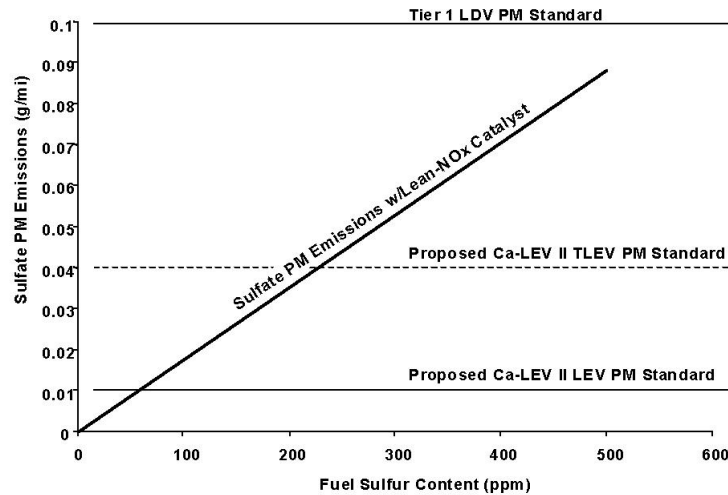


Figure 2-8. Estimated sulfate (primarily H_2SO_4) PM emissions from a LD truck equipped with a low-temperature Pt-zeolite lean- NO_x catalyst system (Wall, 1998).

compounds to be above their minimum detection limits. Because all of these devices incorporate oxidation catalyst functions to some extent, some of the comments related to oxidation catalysts also apply here. One major difference is that some of the aftertreatment devices rely on (lean- NO_x catalyst, NO_x -storage catalyst), or are sometimes assisted by (CRT), the introduction of additional fuel hydrocarbons, either as a reductant or to maintain a high exhaust temperature. The possible species formed from the oxidation or partial oxidation of fuel hydrocarbons have not been determined.

2.2.4. History of Dieselization

2.2.4.1. Dieselization of the On-Road Fleet

Understanding the prevalence of diesel engine penetration into the motor vehicle market is an important aspect of estimating the potential health effects of diesel emissions, past and present. Two classification systems based on rated gross vehicle weight are in use for trucks. These are listed below (Table 2-3).

Table 2-3. Vehicle classification and weights for on-road trucks

Class	Weight (lb)
3	10,001-14,000
4	14,001-16,000
5	16,001-19,500
6	19,501-26,000
7	26,001-33,000
8A ^a	33,001-60,000
8B ^a	>60,000
Medium duty (MD)	10,001-19,500 (same as Classes 3-5)
Light-heavy duty (LHD)	19,501-26,000 (same as Class 6)
Heavy-heavy duty (HHD)	>26,001 (same as Class 7-8)

^aClass 8A and Class 8B are often considered together.

New diesel vehicle sales data for weight classes 5-8 are shown in Figure 2-9 for the years 1957-1998. The number of Class 7 and 8 diesel trucks sold has increased steadily with time while the number of smaller Class 5 and 6 trucks sold peaked in the 1960s and early 1970s and has since decreased. Retail and factory sales data show an increase in the percentage of diesel engines used in trucks sold in Classes 5-8. Using data from factory and retail sales, the percentage of diesel trucks sold by class is shown for the years 1957-1998 in Figure 2-10. The increase in the use of diesel relative to other fuels first occurred for Class 8 trucks. By 1983 more than 97% of the Class 8 trucks sold had diesel engines, according to Navistar and Motor Truck Facts (Bunn, 1999; AAMA Motor Vehicle Facts & Figures, 1983). Before 1980, about 60% of the Class 7 trucks were diesel but very few of the Class 5 and 6 trucks were diesel ($\leq 16\%$ combined). Use of diesel engines in these weight classes increased substantially in the 1980s, with roughly 80% of Class 6 and 67% of Class 7 trucks sold in 1997 being diesel.

Additional insight into dieselization of the on-road fleet can be gained from the 1992 U.S. Census of Transportation (1995). A summary of results is presented in Table 2-4. These data indicate that in 1992 the Class 7 plus Class 8 fleet was 88% diesel. The data presented in Figure 2-10 for the combined fleet in 1992 are in agreement with this value. Dieselization for Class 6 in 1992 was only 37% and for Classes 3-5 only 26%.

The 1992 Census of Transportation also provides information on the model year distribution for vehicles of various weight classes (Figure 2-11). A few 1993 model year

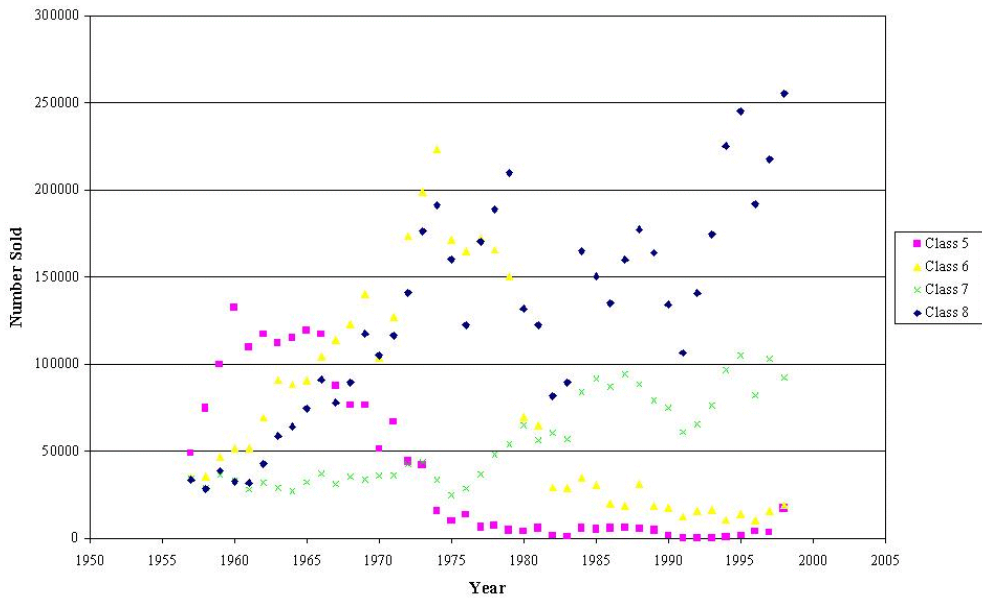


Figure 2-9a. Number of HD diesel trucks sold in years 1957-1998 based on industry sales data.

Source: Bunn (1999).

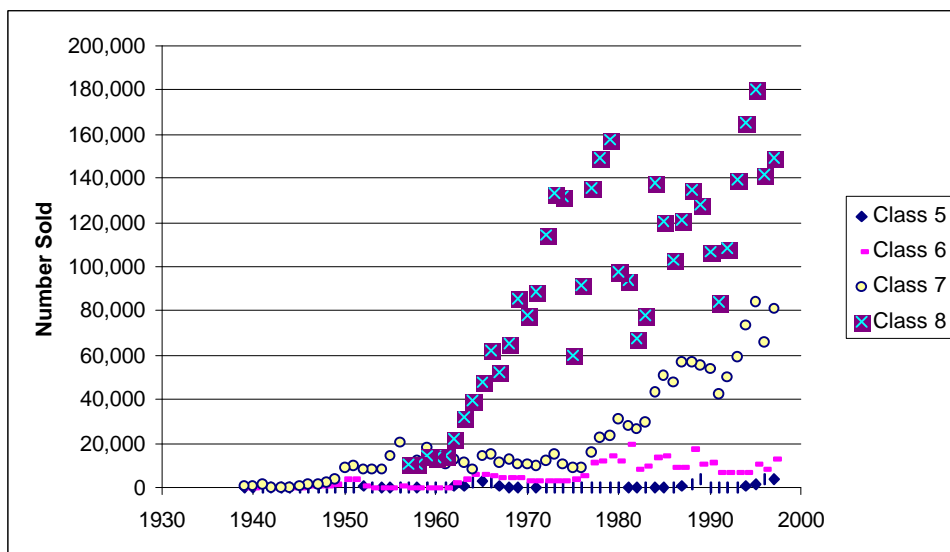


Figure 2-9b. Diesel truck sales (domestic) for the years 1939-1997.
Source: AMA/AAMA Motor Truck Facts.

Table 2-4. Truck fleet results for 1992 from Census of Transportation (1995), results in thousands

Truck class	1992 trucks	1992 diesel	% Diesels
Class 3, 4, and 5 (Medium duty)	1,259.0	326.3	25.9
Class 6 (Light heavy-duty)	732.0	269.7	36.8
Class 7 and 8 (Heavy heavy- duty)	1,966.2	1725.3	87.8

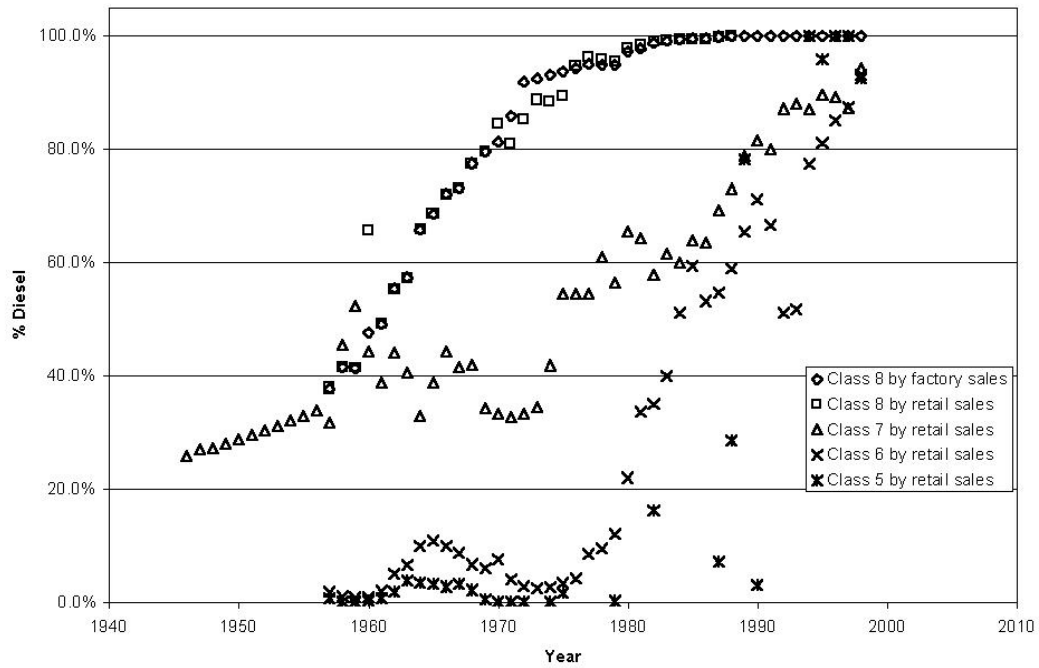


Figure 2-10a. Diesel truck sales as a percentage of total truck sales for the years 1957-1998.
Source: Bunn (1999).

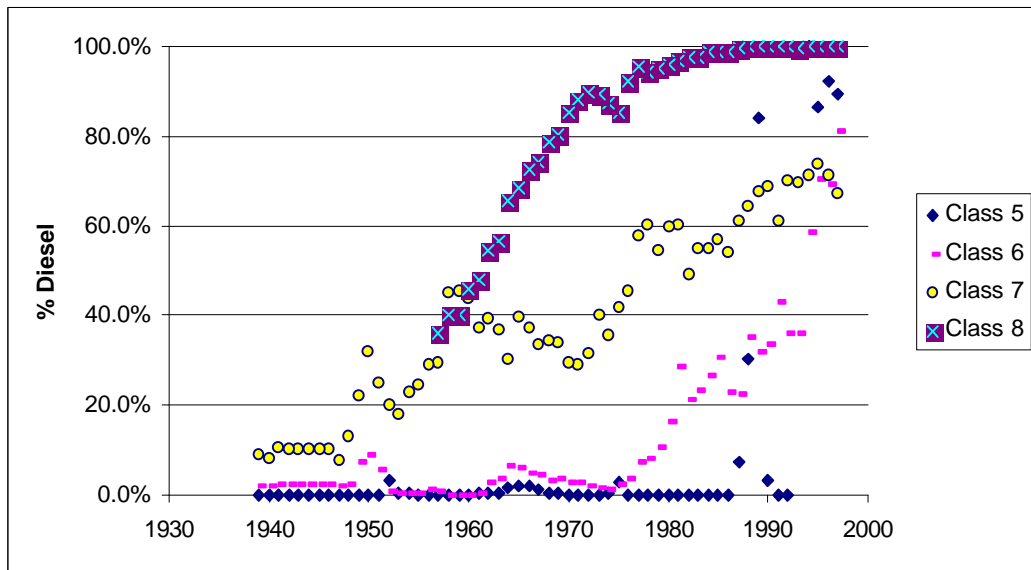


Figure 2-10b. Diesel truck sales as a percentage of total truck sales for the years 1939-1997.

Source: AMA/AAMA Motor Truck Facts.

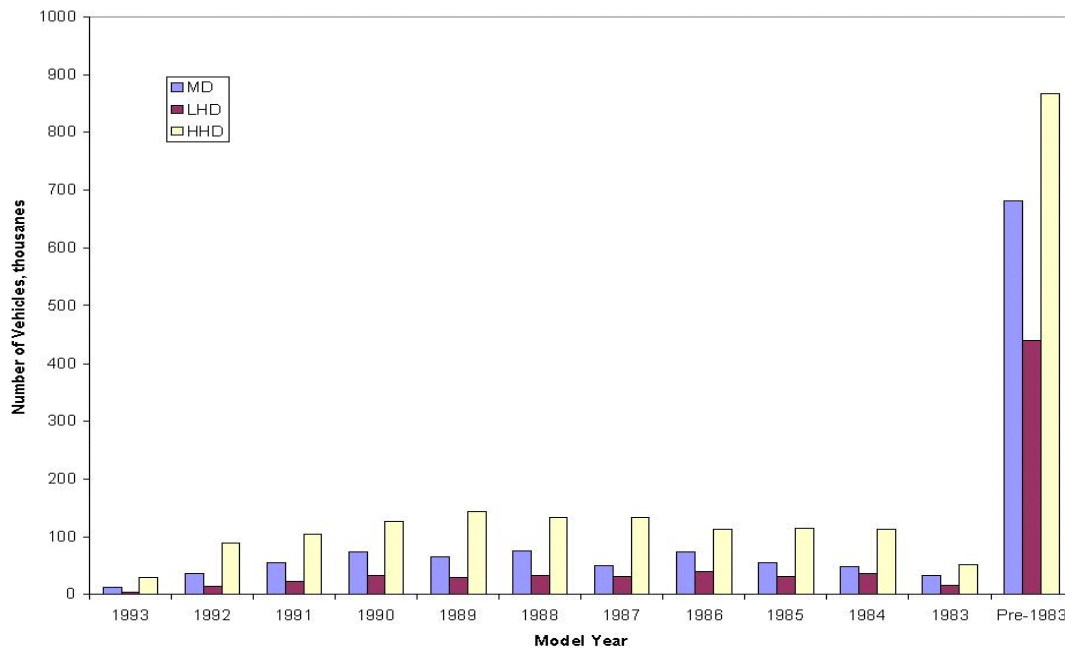


Figure 2-11. Model year distribution of in-use truck fleet in 1992.

Source: Census of Transportation, 1995.

vehicles were in use in 1992. For all three vehicle classes in 1992 there were a large number of vehicles more than 10 years old: 54% for medium duty, 60% for light HD, and 43% for heavy HD. For heavy HD trucks (Classes 7 and 8) there are roughly 100,000 vehicles in each model year from 1983 to 1993. Assuming this is also true before 1983, a large number of trucks (400,000) must be more than 14 years old. This suggests a truck life of around 18 years. The EPA MOBILE5 model assumes a vehicle life of 20 years and MOBILE6 assumes a vehicle life of 25 years, with aging vehicles having fewer vehicle miles traveled on an annual basis (U.S. EPA, 1999a). Motor Truck Facts and later American Automobile Association “Facts and Figures” (AMA, 1927-1975), indicate that 53% of trucks from model years 1947-1956 were still on the road after 14 years and 55% of trucks from model years 1960-1969 were still on the road after 14 years. The proportion of trucks in use after 14 years is 63% for model years 1974-1983, suggesting that the lifespan of trucks built in later years is longer.

In the years since 1950 to 1990 and beyond, vehicle miles traveled by all types of vehicles have increased significantly. For example, Department of Transportation Federal Highway Administration statistics show that passenger car vehicle miles traveled increased from about 400 billion in 1951 to 1,400 billion in 1995 and 1,500 billion in 1997, an increase of about 360% and 380% for these years compared to 1951. Meanwhile, vehicle miles traveled by combination trucks increased from about 20 billion in 1951 to 94,000 billion in 1990 and 124,500 billion in 1997, a somewhat larger increase of 470% and 620% for these years compared to 1951. These data highlight the fact that combination truck usage has increased more than passenger car usage from the early 1950s to the 1990 and 1997 time frame. The Department of Transportation statistics are also available for other vehicle categories such as lighter trucks.

The EPA MOBILE5 and PART5 models calculate that about 2.6% of total vehicle miles traveled in the 1950 time frame came from diesels with a gross vehicle weight over 33,000 pounds (Classes 7 and 8). In 1990, about 3.3% of total vehicle miles traveled came from diesel trucks in these weight categories. In the 1950-1990 time frames and beyond, diesel trucks are responsible for an increasing fraction of the vehicle miles traveled.

2.2.4.2. Dieselization of Railroad Locomotive Engines

Early in the 20th century the political and economic pressure on the railroads to replace steam locomotives was substantial. Railroads were losing business to other forms of transport. The diesel-electric locomotive provided 90% in-service time compared to only 50% for steam locomotives, and had three times the thermal efficiency (Klein, 1991; Kirkland, 1983). Additionally, several cities had passed laws barring steam locomotives within the city limits because the large quantities of smoke obscured visibility, creating a safety hazard. The first prototype diesel locomotive was completed in 1917. By 1924 General Electric was producing a

standard line of switching locomotives on a production basis. Electro-Motive Corporation was founded the same year to produce diesel locomotives in competition with GE. This company was purchased in 1929 by General Motors and became the Electro-Motive Division. After this acquisition, GM began to develop the 2-stroke engine for this application. Up to this time, all locomotive diesel engines were 4-stroke. Two-strokes offered a much higher power-to-weight ratio and GM's strategy was to get a large increase in power by moving to the 2-stroke cycle. The first true high-speed, 2-stroke diesel-electric locomotives were produced by GM in 1935. However, because of the economic climate of the Great Depression few of these were sold until after the Second World War. At the end of the war most locomotives were still steam-driven but were more than 15 years old, and the railroads were ready to replace the entire locomotive fleet. Few if any steam locomotives were sold after 1945 as the entire fleet was converted to diesel (Coifman, 1994).

The locomotive fleet has included significant percentages of both 2- and 4-stroke engines. The 4-stroke diesel engines were naturally aspirated in the 1940s and 1950s. It is unlikely that any of the 2-stroke engines used in locomotive applications were strictly naturally aspirated. Nearly all 2-stroke diesel locomotive engines are uniflow scavenged, with a positive-displacement blower for scavenging assistance. In 1975, it was estimated that 75% of the locomotives in service were 2-stroke, of which about one-half used one or more turbochargers in addition to the existing positive-displacement blower for additional intake boost pressure.

Almost all of the 4-stroke locomotive engines were naturally aspirated in 1975 (Hare and Springer, 1972). Electronic fuel injection for locomotive engines was first offered in the 1994 model year (U.S. EPA, 1998b). All locomotive engines manufactured in recent years are turbocharged, aftercooled or intercooled 4-stroke engines. In part, this is because of the somewhat greater durability of 4-strokes, although impending emissions regulations may have also been a factor in this shift. The typical lifespan of a locomotive has been estimated to be more than 40 years (U.S. EPA, 1998b). Many of the smaller railroads are still using engines built in the 1940s, although the engines may have been rebuilt several times since their original manufacture.

2.2.4.3. Historical Trends in Diesel Fuel Use and Impact of Fuel Properties on Emissions

Use of diesel fuel has increased steadily in the second half of this century. According to statistics from the Federal Highway Administration (1995; 1997a), in 1949 diesel fuel was approximately 1% of the total motor fuel used, and in 1995 it was about 18%. Over the same time diesel fuel consumption increased from about 400 million gallons to 26 billion gallons per year in the United States, an increase by a factor of more than 75 (Figures 2-12 and 2-13).

The chemistry and properties of diesel fuel have a direct effect on engine emissions. Researchers have studied the effect of sulfur content, total aromatic content, polyaromatic

content, fuel density, T90/T95, oxygenate content, and cetane. Lee et al. (1998) have comprehensively reviewed literature studies of the effect of these fuel properties on regulated emissions. Their conclusions were based on fleet and multiple engine tests conducted over both transient and steady-state cycles, and were limited to studies in which the effects of the various fuel characteristics could be decoupled from each other. Sulfur content, cetane number, density, total aromatics and polyaromatics content, as well as boiling point distribution can have an impact on emissions. It was concluded that the effect of most fuel changes on modern engines is less than the effect on older, higher emitting engines.

Most important for emissions, the chemical makeup of diesel fuel has changed over time, in part because of new regulations. EPA currently regulates diesel fuel and requires sulfur content to be less than 500 ppm for on-road applications, and that cetane index (a surrogate for actual measurements of cetane number) be greater than or equal to 40, or the maximum aromatic content to be 35% or less (CFR 40:80.29). California has placed additional restrictions on the cetane number and aromatic content of diesel fuel (California Code of Regulations, Title 13).

Prior to 1993, diesel fuel sulfur levels were not federally regulated in the United States. Only recommended industry practices were in place (e.g., the ASTM D 975 specified 0.5% fuel sulfur limit). During the years 1960 to 1986, fuel sulfur content showed no chronological increasing or decreasing trends and ranged from 0.23-0.28wt%, while the average cetane number of U.S. diesel fuel declined steadily from 50.0 to 45.1, or about 0.2 per year (NIPER, 1986). Based on a linear regression analysis, the average cetane number was 52.2 in 1949 and 46.8 in 1976. This declining trend in cetane number was likely accompanied by an increase in aromatic content and density (Lee et al., 1998). The reason for the decline was that as diesel demand grew, straight-run diesel became a smaller part of the pool and light-cycle oil from catalytic cracking became important. Light-cycle oil is high in aromatics. One study measuring the impact of changes in cetane number and aromatic content found that increasing the aromatic content from 20% to 40%, with an accompanying decrease in the cetane number from 53 to 44 resulted in a 4% increase in NO_x and a 7% increase in PM (McCarthy et al., 1992). These values can be considered reasonable upper bounds for the small effect changes in fuel quality likely had on NO_x and PM emissions during the years 1949-1975.

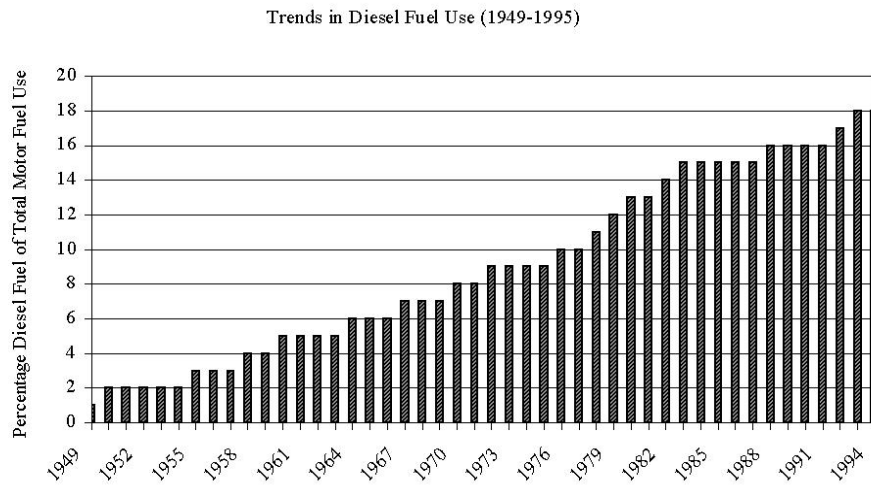


Figure 2-12. Diesel fuel use since 1949.

Source: Federal Highway Administration, 1995.

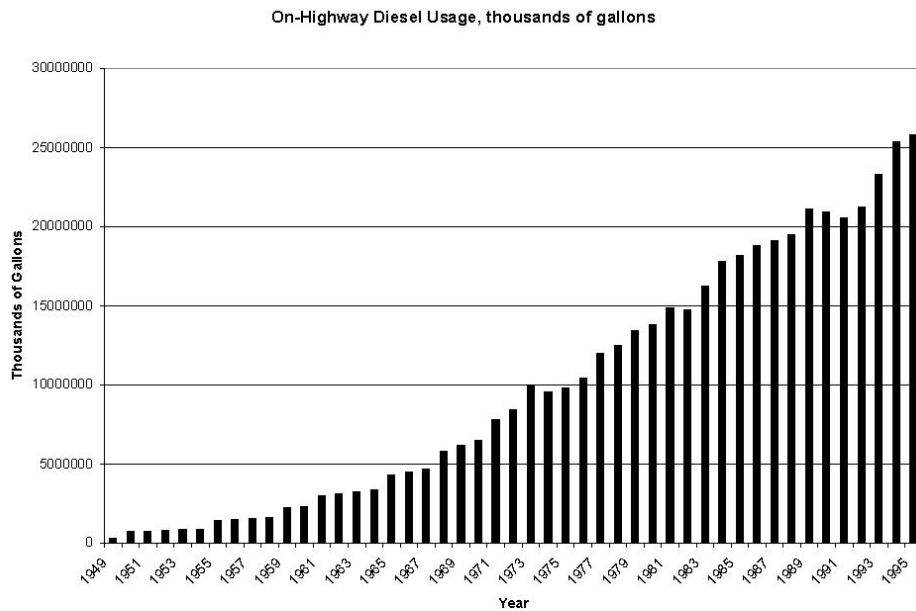


Figure 2-13. On-highway diesel fuel consumption since 1949, values in thousands of gallons.

Source: Federal Highway Administration, 1995.

1 In wintertime, on-road No. 2 diesel may contain some percentage (~15% or more) of No.
2 1 diesel to improve cold flow properties. Blending of No. 1 may also lower the aromatic content,
3 resulting in improved emissions performance. Thus, there may also be some small but perceptible
4 seasonal changes in emissions from diesel engines.

5 A maximum allowable fuel sulfur content in the United States for on-road diesel fuel was
6 established at 0.05 mass % in 1993 in advance of a new 0.10 g/bhp-hr PM standard for HD on-
7 highway trucks. This reduced total PM emissions through reduction of sulfate PM (primarily
8 present as sulfuric acid). Approximately 1% to 4 % of fuel sulfur is oxidized to SO₃, which forms
9 sulfuric acid in the presence of water vapor in the exhaust (Wall et al., 1987; Khatri et al., 1978;
10 Baranescu, 1988). Considerably higher sulfuric acid PM emissions are possible with diesel
11 exhaust aftertreatment systems containing precious metals (oxidation catalysts, lean NO_x catalysts,
12 catalyzed PM traps). At temperatures over 350 to 500 °C (depending on device), SO₂ in the
13 exhaust can be oxidized to SO₃ and increase sulfuric acid PM emissions (McClure et al., 1992;
14 McDonald et al., 1995; Wall, 1998). Sulfur content remains at unregulated levels for off-highway
15 diesel fuels. Nationally, on-road fuels averaged 0.032% sulfur in 1994 while off-highway fuels
16 averaged 0.322% (Dickson and Sturm, 1994).

18 **2.2.5. Chronological Assessment of Emission Factors**

19 **2.2.5.1. On-Road Vehicles**

20 Historically, measured emissions from HD diesel vehicles have been widely variable.
21 However, certain chronological trends can be identified, driven primarily by tightening regulatory
22 standards since the mid-1970s. Prior to that time, changes in average fuel composition and engine
23 technologies were implemented for reasons other than emissions control. Although there is a
24 reasonable amount of data upon which to base an emission factor for late 1970s and later engines,
25 there are virtually no transient test data available to EPA on engines earlier than the mid-1970s.
26 Nevertheless, there are some factors that help lead to conclusions about the emissions of these
27 engines. Diesel truck engine technology changed little in this time frame, and over this whole
28 period used roughly the same means of tuning the engine's air-fuel ratio; that is, tuning was done
29 to not permit air-fuel ratios richer than the "smoke limit" of about 22:1. This tuning, in essence,
30 formed an "upper limit" on particulate emissions and was done before EPA smoke standards (for
31 customer satisfaction reasons). There is only qualitative correlation between smoke and
32 particulate emissions over the transient driving cycle, but there is semiquantitative correlation
33 between smoke and particulates over steady-state operating modes (McGuckin and Rykowski,
34 1981). The fact that engines, turbocharged or not, were tuned to avoid smoky operation makes it
35 reasonable to assume that they had emissions roughly at the mid-1970s level. Other than the
36 increased use of turbochargers, HD diesel engine technology was reasonably stable. Thus, it is

reasonable to conclude that the emission factors developed above for mid-1970s (and later) engines adequately represent the engines in use in the 1950-1970 time frame.

There have been numerous studies of emissions from in-use on-road HD (greater than 8,500 lbs GVWR) diesel vehicles. Emissions of regulated pollutants from these studies have been reviewed (Yanowitz et al., 1999b) and the review findings, which encompass vehicles from model years 1976 to 1998, are summarized below.

Figures 2-14 through 2-16 below show chassis dynamometer data from more than 200 different vehicles, reported in 20 different published studies (approximately half of which are from transit buses) (Yanowitz et al., 1999a; Warner-Selph and Dietzmann, 1994; Dietzmann et al., 1980; Graboski et al., 1998a; McCormick et al., 1999; Clark et al., 1997; Bata et al., 1992; Brown and Rideout, 1996; Brown et al., 1997; Clark et al., 1995; Dunlap et al., 1993; Ferguson et al., 1992; Gautam et al., 1992; Katragadda et al., 1993; Rideout et al., 1994; Wang et al., 1993; Wang et al., 1994; Williams et al., 1989; Whitfield and Harris, 1998), as well as a large amount of additional data collected by West Virginia University and available on the World Wide Web at www.afdc.nrel.gov. The results from vehicles tested more than once using the same test cycle, and without any additional mileage accumulated between tests, are averaged and reported as one data point. Emissions results from vehicles tested under different test cycles or at different points in the engine's life cycle have been reported as separate data points. Note that all NO_x mass emissions data are reported as equivalent NO₂.

Figures 2-14 through 2-16 show emissions trends for NO_x, PM, and HC in g/mile. A least-squares linear regression is plotted on each graph and yields the following equations for predicting emissions trends (applicable to the years 1976-1998):

$$\text{Log NO}_x \text{ (g/mile)} = (\text{Model year} * -0.008) + 16.519 \quad (2-1)$$

$$\text{Log PM (g/mile)} = (\text{Model year} * -0.044) + 88.183 \quad (2-2)$$

$$\text{Log HC (g/mile)} = (\text{Model year} * -0.055) + 109.390 \quad (2-3)$$

As shown in Figures 2-14, 2-15, and 2-16, which include 95% confidence limits and regression lines, changes in NO_x emissions have been relatively small, with an emission rate averaging about 26 g/mile. PM, CO, and THC emissions, though widely variable within any model year, have shown a pronounced declining trend. PM emissions from chassis dynamometer tests decreased from an average 3.0 g/mi in 1977 to 0.47 g/mi in 1997, suggesting a decrease in PM emissions of a factor of 6. Although it is clear that emissions of CO, HC, and

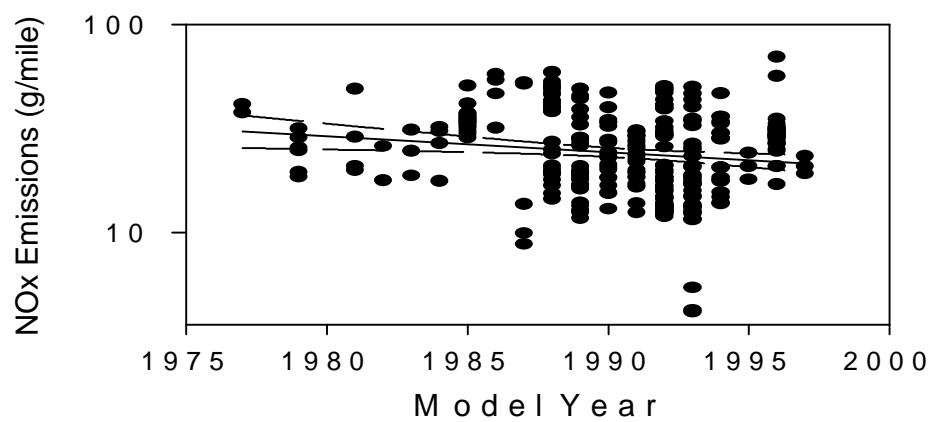


Figure 2-14. Model year trends in NO_x emissions (g/mile).

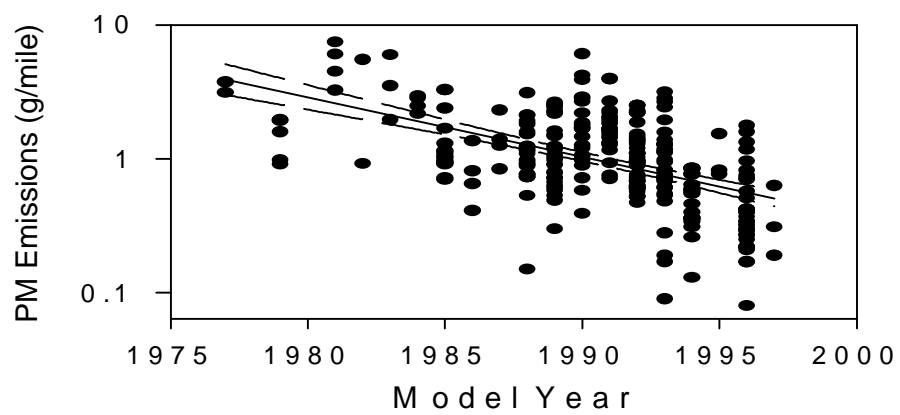


Figure 2-15. Model year trends in PM emissions (g/mile).

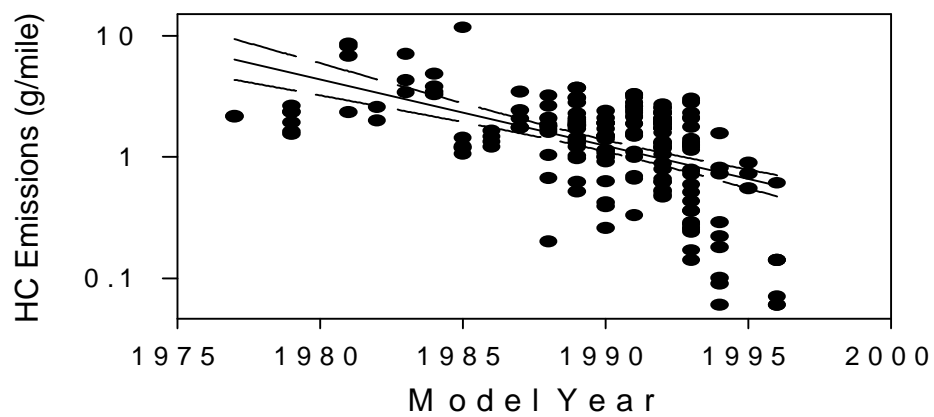


Figure 2-16. Model year trends in HC emissions (g/mile).

PM have declined significantly since the early 1970s, emissions of NO_x have remained approximately constant.

Other approaches for measuring emissions from in-use, on-road diesel vehicles include remote sensing and tunnel tests. The literature reports of those studies are summarized in Tables 2-5 and 2-6. Gram-per-mile emission factors vary substantially for the various tunnels, with NO_x ranging from 9 to 24 g/mile, PM ranging from 0.6 to 1.8 g/mile, CO ranging from 6 to 14 g/mile, and THC ranging from 0.16 to 2.55 g/mile. Remote sensing produces results in terms of pollutant emissions per unit of fuel, not on a per-mile basis. On a g/gallon of fuel consumed basis, agreement between the studies for NO_x emissions is reasonably good, suggesting an average level for the fleet of about 130 g/gal for both tunnel tests and remote sensing, comparable to the average emissions factor generated from chassis dynamometer studies. Generally, chassis dynamometer tests and engine dynamometer test results are corrected for ambient humidity in accordance with the Federal Test Procedure (CFR 40, Subpart N). Tunnel tests and remote sensing tests have typically not included corrections for humidity. Appropriate humidity corrections for NO_x and PM can be greater than 20% and 10%, respectively (or a total difference of more than 45% and 20% between low- and high-humidity areas), under normally occurring climatic conditions. Additionally, the remote sensing literature has not addressed how to determine the correct value for the NO/NO_x ratio, and there is reason to believe that this value may differ systematically from site to site although, again, most of the NO_x is NO.

There are no reported instances of HD diesel PM measurement by remote sensing, but there were several tunnel tests that measured PM. In addition to the humidity correction discussed above, several factors must be taken into account when comparing PM measurements from tunnel tests to the chassis dynamometer measurements (Yanowitz et al., 1999b): (1) Chassis dynamometer testing measures only tailpipe emissions; tunnel tests include emissions from other sources (tire wear, etc). (2) Tunnel tests typically measure emissions under steady-speed freeway conditions, whereas most chassis dynamometer tests are measured on cycles that are more representative of stop-and-go urban driving conditions. This latter limitation also applies to remote sensing readings, which measure instantaneous emissions versus emissions over a representative driving cycle. PM is emitted from HD vehicles at the greatest rate during accelerations.

Because THC emissions for diesel vehicles are very low in comparison to gasoline vehicles, tunnel test results for THC have a high degree of uncertainty. A regression analysis to determine the contribution of the limited number of HD vehicles to THC emissions is somewhat unstable, i.e., small errors in the total measurements can change estimates. Similarly, CO emissions are comparable to automobile emissions on a per-vehicle-mile basis, but since there

Table 2-5. Emissions results from tunnel tests (adapted from Yanowitz et al., 1999b)

Test	Tunnel Location	Fuel efficiency (mi/gal)	NO _x ^a (g/mi)	NMHC (g/mi)	CO (g/mi)	PM (g/mi)	CO ₂ (g/mi)	NO _x ^a (g/gal)	NMHC (g/gal)	CO (g/gal)	PM (g/gal)
Pierson and Brachaczeck, 1983	Allegheny, 1970-74 Allegheny, 1975 Allegheny, 1976 Allegheny, 1976 Tuscarora, 1976 Tuscarora, 1976 Allegheny, 1977 Allegheny, 1979 Allegheny, 1979	5.42 ^b				.90-1.80 1.75 +/- .19 1.5 +/- .10 1.4 +/- .07 1.3 +/- .19 1.39 +/- .26 1.3 +/- .08 1.2 +/- .03 1.4 +/- .04					4.9-9.8 9.49 +/- 1.03 8.1 +/- .54 7.6 +/- .4 7.0 +/- 1.0 7.5 +/- 1.40 7.0 +/- .43 6.5 +/- .16 7.6 +/- .19
Rogak et al., 1998	Cassiar Tunnel, 1995, Vancouver	8.03 ^b	19.50 +/- 4.22	-0.16 +/- 0.88	6.79 +/- 11.78		1280 +/- 40	157 +/- 34	-1 +/- 7	55 +/- 95	
Miguel et al., 1998	Caldecott Tunnel, 1996, San Francisco	5.42 ^c	23.82 +/- 4.17			1.67 +/- 0.24 ^d		129 +/- 23			9.0 +/- 1.3 ^d
Weingartner et al., 1997	Gubrist Tunnel, 1993, Zurich	5.60 ^c				0.62 +/- 0.02 ^f					3.5 +/- 0.1 ^f
Pierson et al., 1996	Fort McHenry Tunnel, downhill, 1992, Baltimore	11.46 ^b	9.66 +/- 0.32	0.92 +/- 0.21	6.8 +/- 1.5		897 +/- 48	111 +/- 4	11 +/- 2	78 +/- 17	
Pierson et al., 1996	Fort McHenry Tunnel, uphill, 1992, Baltimore	5.42 ^b	22.50 +/- 1.00	2.55 +/- 1.05	14.3 +/- 5.5		1897 +/- 168	122 +/- 5	14 +/- 6	78 +/- 30	
Pierson et al., 1996	Tuscarora Tunnel 1992, Pennsylvania	6.44 ^b	19.46 +/- 0.85	0.68 +/- 0.20	6.03 +/- 1.61		1596 +/- 78	125 +/- 5	4 +/- 1	39 +/- 10	
Kirchstetter et al., 1999	Caldecott Tunnel, 1997, San Francisco	5.42 ^c	23.82 +/- 2.98			1.43 +/- 0.12 ^g		129 +/- 16			7.7 +/- 0.6 ^g

^aNO_x reported as NO₂.^bCalculated from observed CO₂ emissions assuming fuel density 7.1 lb/gal and C is 87% of diesel fuel by weight.^cSince CO₂ emissions not available, fuel efficiency assumed to be the same as in slightly uphill tunnel (Fort McHenry).^dReported as black carbon, assumed that 50% of total PM emissions are BC.^eSlope of tunnel unknown, so used average fuel efficiency for the United States.^fPM₃.^gPM_{2.5}.^hUncertainty reported as +/-1.0 standard deviation, except where literature report did not specify standard deviation; in those cases uncertainty listed as reported.

Table 2-6. Remote sensing results for hd vehicles (Yanowitz et al., 1999b)

	Reference	Year study conducted	Emissions (g/gal)
NO _x (reported as NO ₂)	Jimenez et al., 1998	1997	150 ^{a,b,c}
	Cohen et al., 1997	1997	108 ^{a,b,c}
	Countess et al., 1999	1998	187 ^{a,b,c}
CO	Bishop et al., 1996	1992	59 ^b
	Cohen et al., 1997	1997	54 ^b
	Countess et al., 1999	1998	85 ^b
THC	Bishop et al., 1996	1992	0.002 HC/CO ₂ mole ratio ^d
	Cohen et al., 1997	1997	0.00073 HC/CO ₂ mole ratio ^d

^aRemote sensing measures NO. The reported value was corrected to a NO_x (as NO₂) value by assuming 90% (mole fraction) of NO_x is NO.

^bEmissions in g/gal calculated by assuming that fuel density is 7.1 lb/gal and C is 87% by weight of fuel.

^cNo humidity correction factor is included.

^dIn order to calculate emissions in g/gal, an average molecular weight is needed.

are generally many more automobiles than HD diesels in tunnel tests, CO measurements may be associated with a high degree of uncertainty.

Given the variability between testing methods, and assuming the on-road fleet measured in tunnel and remote sensing tests is primarily vehicles 0 to 10 years old, there is reasonable comparability between chassis dynamometer results and average tunnel and remote sensing results for PM, CO, and HC. Neither tunnel testing nor remote sensing results show any pronounced chronological trends for these regulated pollutants, primarily because virtually all of the testing was done over a short period in the 1990s. The average model year for HD vehicles was reported in only one case (Kirchstetter et al., 1999) and was found to be 1988 for a tunnel test conducted in 1997. However, even in the case of tunnel testing, measurements of PM from the 1970s PM levels are not significantly different from what was measured in the 1990s.

The data on regulated emissions do allow a comparison of emissions from 2- and 4-stroke engines for PM (Figure 2-17). It is clear that there is no significant difference in PM mass emissions for 2- and 4-stroke engines over the time period covered. This is true even in 1993. In model year 1994 there were no on-road 2-stroke engines. Similarly, no significant difference was observed for emissions of HC, CO, or NO_x.

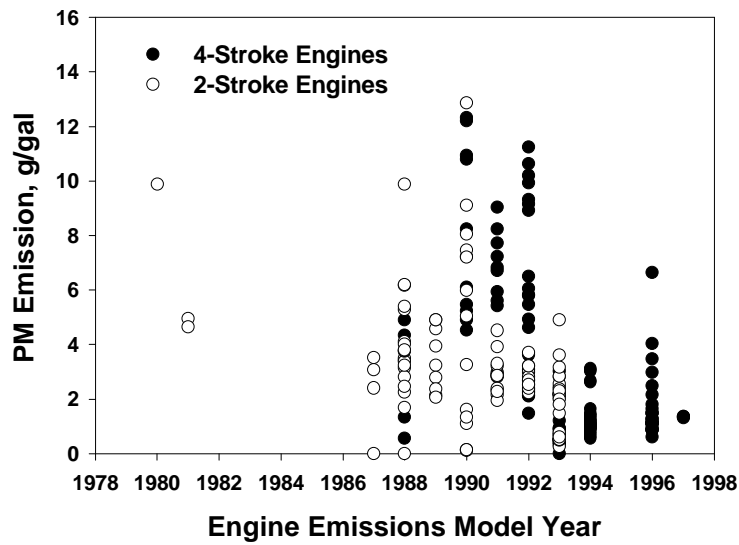
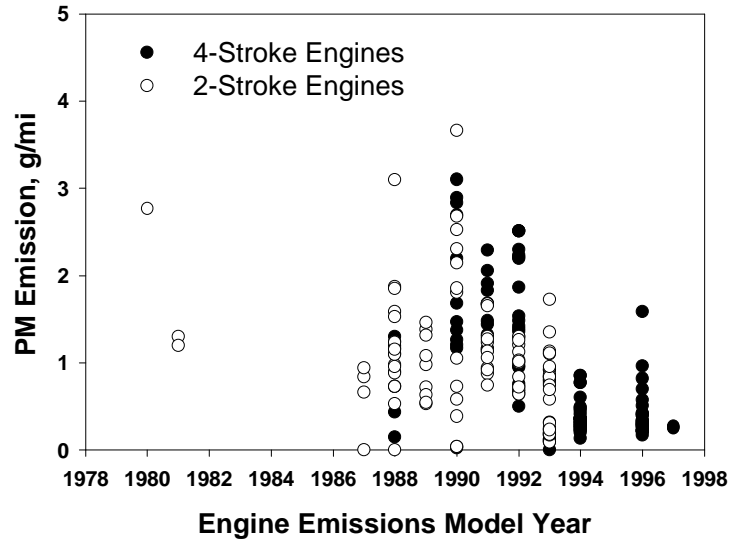


Figure 2-17. Comparison of 2-stroke and 4-stroke engines PM emissions on a g/mi and g/gal basis (low altitude data only).
 Source: Yanowitz et al., 1999b.

2.2.5.2. Locomotives

Locomotive engines generally range from 1000 horsepower up to 6000 horsepower. Similar to the much smaller truck diesel engines, the primary pollutants of concern are NO_x, PM, CO, and HC. Unlike truck engines, most locomotive engines are not mechanically coupled to the drive wheels. Because of this decoupling, locomotive engines operate in specific steady-state modes rather than the continuous transient operation normal for trucks. Because the locomotive engines operate only at certain speeds and torques, the measurement of emissions is considerably more straightforward for locomotive engines than for truck engines. Emissions measurements made during the relatively brief transition periods from one throttle position to another indicate that transient effects are very short and thus could be neglected for the purposes of overall emissions estimates.

Emissions measurements are made at the various possible operating modes with the engine in the locomotive, and then weighting factors for typical time of operation at each throttle position are applied to estimate total emissions under one or more reasonable operating scenarios. In the studies included in this analysis, two scenarios were considered: line-haul (movement between cities or other widely separated points) and switching (the process of assembling and disassembling trains in a switchyard).

The Southwest Research Institute made emissions measurements for three different engines in locomotives in 1972 (Hare and Springer, 1972) and five more engines in locomotives using both low- and high-sulfur fuel in 1995 (Fritz, 1995). Two engine manufacturers (the Electromotive Division of General Motors, or EMD, and the General Electric Transportation Systems, or GETS) tested eight different engine models and reported the results to EPA (U.S. EPA, 1998b). There are also additional data. All available data on locomotives are summarized in the regulatory impact assessment and shown in Figure 2-18.

2.2.6. Physical and Chemical Composition of Particles

Diesel PM is defined by the measurement procedures summarized in Title 40 CFR, Part 86, subpart N. These procedures define PM emissions as the mass of material collected on a filter at a temperature of 52°C or less after dilution of the exhaust. As the exhaust is diluted and cooled, nucleation, condensation, and adsorption transform volatile material to solid and liquid PM. Diesel exhaust particles are aggregates of primary spherical particles consisting of solid carbonaceous material and ash, and which contain adsorbed organic and sulfur compounds (sulfate) combined with other condensed material. The organic material includes unburned fuel, lube oil, and partial combustion and pyrolysis products. This is frequently quantified as the soluble organic fraction, or SOF. The SOF can range from less than 10% to more than 90% by

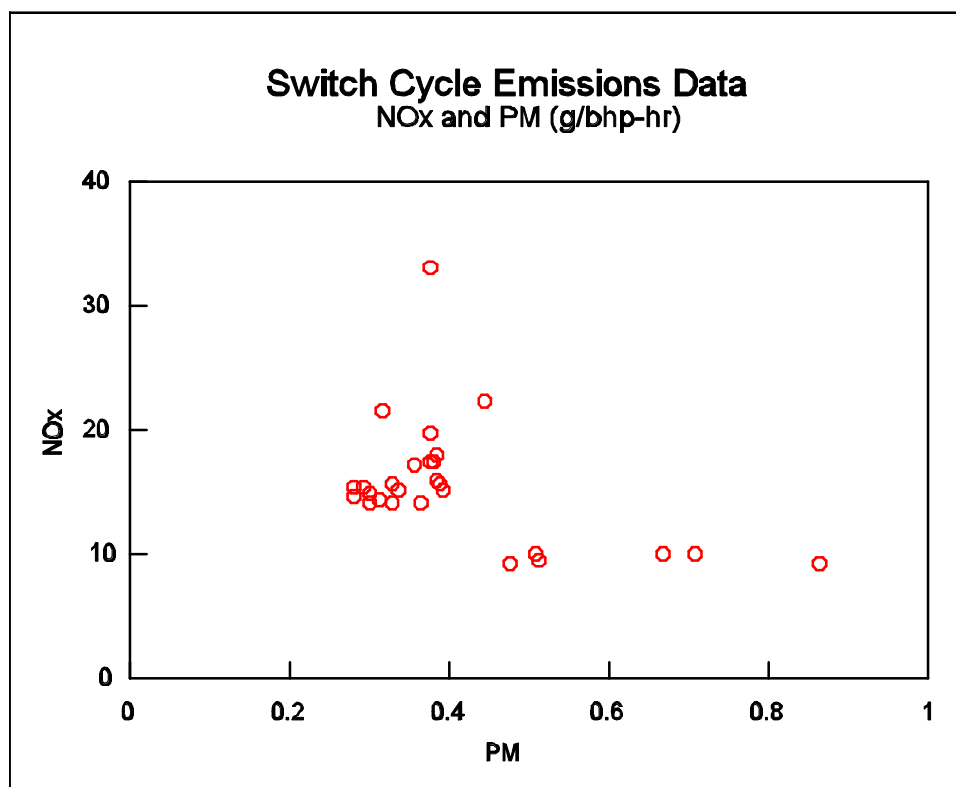
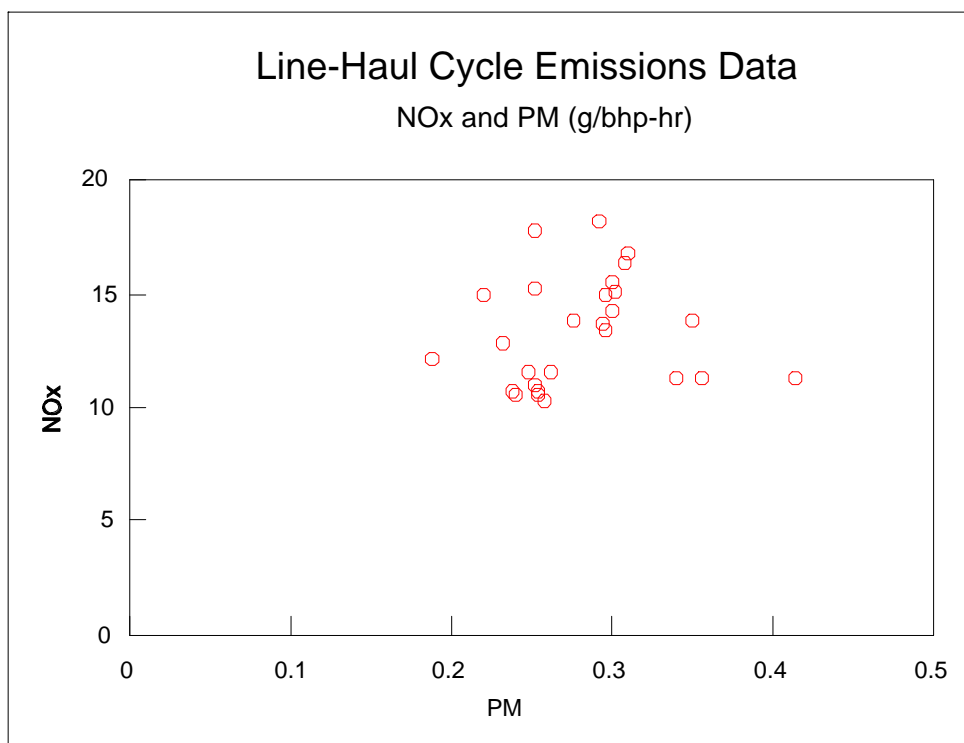


Figure 2-18. Line-haul and switch emissions data.

Source: U.S. EPA, 1998a.

1 mass, with the highest values occurring at light engine load where exhaust temperature is low
2 (Kittelson, 1998). The SOF fraction can also vary with engine design, with high lube oil emitting
3 older engines producing higher SOF. Sulfate depends on fuel sulfur content primarily.

4 Carbonaceous diesel particulate matter has a high specific surface area (30-50 m²/g) (Frey
5 and Corn, 1967). Because of this high surface area diesel particles are able to adsorb large
6 quantities of organic materials. After removal of the organic material by extraction, the surface
7 area increases to as high as 90 m²/g (Pierson and Brachaczek, 1976). A variety of solvents have
8 been used to extract the SOF (Levson, 1988). Soxhlet extraction with a binary solvent consisting
9 of an aromatic and an alcohol appears to give the best recovery of PAHs, although
10 dichloromethane is also used. Some studies have then used liquid chromatography to separate the
11 extract into various fractions on the basis of chemical composition and polarity.

12 The distribution of emissions between the gas and particle phases in diesel exhaust
13 (gas/particle partitioning) is determined by the vapor pressure of the individual species, the type
14 and amount of particulate matter present (surface area available for adsorption), and the
15 temperature (Zielinska et al., 1998). Two-ring and smaller compounds exist primarily in the gas
16 phase while five-ring and larger compounds are completely adsorbed on the particles. Three- and
17 four-ring compounds are distributed between the two phases. Some studies use sampling trains
18 designed to collect both gas-phase and particle-phase compounds, while others simply report the
19 amount or emission of a given compound in the PM SOF. During the collection of particulate
20 and organic compounds, filter adsorption, blow-off (loss from the filter), and chemical
21 transformation of the semivolatile compounds have been reported to occur (Schauer et al., 1999;
22 Cantrell et al., 1986; Feilberg et al., 1999; Cautreels and Cauwenberghe, 1978).

23 For diesel engine emissions, approximately 57% of the extracted organic mass is contained
24 in the nonpolar fraction (Schuetzle, 1983). About 90% of this fraction consists of aliphatic
25 hydrocarbons from approximately C₁₄ to about C₄₀ (Black and High, 1979; Pierson et al., 1983).
26 Polycyclic aromatic hydrocarbons and alkyl-substituted PAHs account for the remainder of the
27 nonpolar mass. The moderately polar fraction (~9% w/w of extract) consists mainly of
28 oxygenated PAHs species, substituted benzaldehydes, and nitrated PAHs. The polar fraction
29 (~32% w/w of extract) is composed mainly of n-alkanoic acids, carboxylic and dicarboxylic acids
30 of PAHs, hydroxy-PAHs, hydroxynitro-PAHs, nitrated N-containing heterocyclic compounds,
31 etc. (Schuetzle, 1983; Schuetzle et al., 1985).

32 Rogge et al. (1993) reported the composition of the extractable portion of fine particulate
33 matter emitted from two HD diesel trucks (1987 model year). No HPLC separation step was
34 employed and the extract (hexane followed by benzene/2-propanol) was analyzed by capillary gas
35 chromatography/mass spectrometry (GC/MS) before and after derivatization. The unresolved
36 organic mass, which comprises 90% of the elutable organic mass, consists mainly of branched and
37 cyclic hydrocarbons. From the mass fraction that is resolved as discrete peaks by GC/MS, ~42%

1 was identified as specific organic compounds. Most of the identified resolved organic mass
2 (~60%) consists of n-alkane, followed by n-alkanoic acids (~20%). PAHs account for ~3.5%
3 and oxy-PAHs (ketones and quinones) for another ~3.3%. Taking into account the differences in
4 the analytical procedures and the percentage of identified peaks, this distribution is roughly similar
5 to those reported by Schuetzle (1983).
6

7 **2.2.6.1. SOF and Elemental Carbon Content of Particles**

8 Chassis dynamometer results indicate that SOF emissions have trended downward over
9 the years as engine manufacturers have tried to reduce oil consumption. This is shown in Figure
10 2-19, where the trend can be seen as both reduction in SOF weight percent and in SOF g/mi
11 emissions. The downward trend is driven primarily by the need to reduce oil consumption, and
12 thereby reduce engine wear and maintenance costs, as well as the need to meet PM emission
13 standards. There is no significant difference in SOF emissions from 2- and 4-stroke engines in
14 later years, while 2-stroke engines in the 1970s tended to emit greater amounts of SOF compared
15 with typical 4-stroke engines. The downward trend in SOF as a percentage indicates that the
16 solid carbonaceous material as a percentage of PM has been increasing. Figure 2-20 shows the
17 PM solids g/mile emissions (TPM-SOF) for several vehicles tested on chassis dynamometers. A
18 decreasing trend in PM solids is also evident, consistent with the observed decline in total PM
19 emissions. It is tempting to assume that this solid carbonaceous portion is approximately the
20 same as elemental carbon (EC, a quantity not commonly measured in HD studies). This
21 assumption is validated, to a good approximation, by a study in which both SOF and EC were
22 measured (SOF measured by Yanowitz and co-workers [1999a] and EC measured on the same
23 samples by Zielinska and co-workers [1998]); a parity plot of these results is shown in Figure 2-
24 21. The data reported by Zielinska and co-workers currently appear to be the only measurements
25 of EC for in-use vehicles. These data are for 4-stroke engines. EC ranged from 31% to 84% of
26 PM, and averaged 63%. It is apparent from Figure 2-20 that g/mile EC emissions have declined
27 with model year.

28 Engine testing studies show SOF percentage to be highly variable, ranging from 20% to
29 60%, and exhibiting a declining trend with model year (McCarthy et al., 1992; Springer, 1979;
30 Johnson et al., 1994; Bagley et al., 1998; Tanaka et al., 1998; Rantanen et al., 1993; Mitchell et
31 al., 1994; Hansen et al., 1994). On a g/bhp-h basis SOF emissions declined significantly in the
32 early 1990s and are typically in the range of 0.02-0.05 g/bhp-h. Engine dynamometer data
33 provide confirmation that total SOF and PM solids (or EC) emissions have declined. Note that
34 there are many more engine testing studies available, which this document does not attempt to
35 comprehensively review.

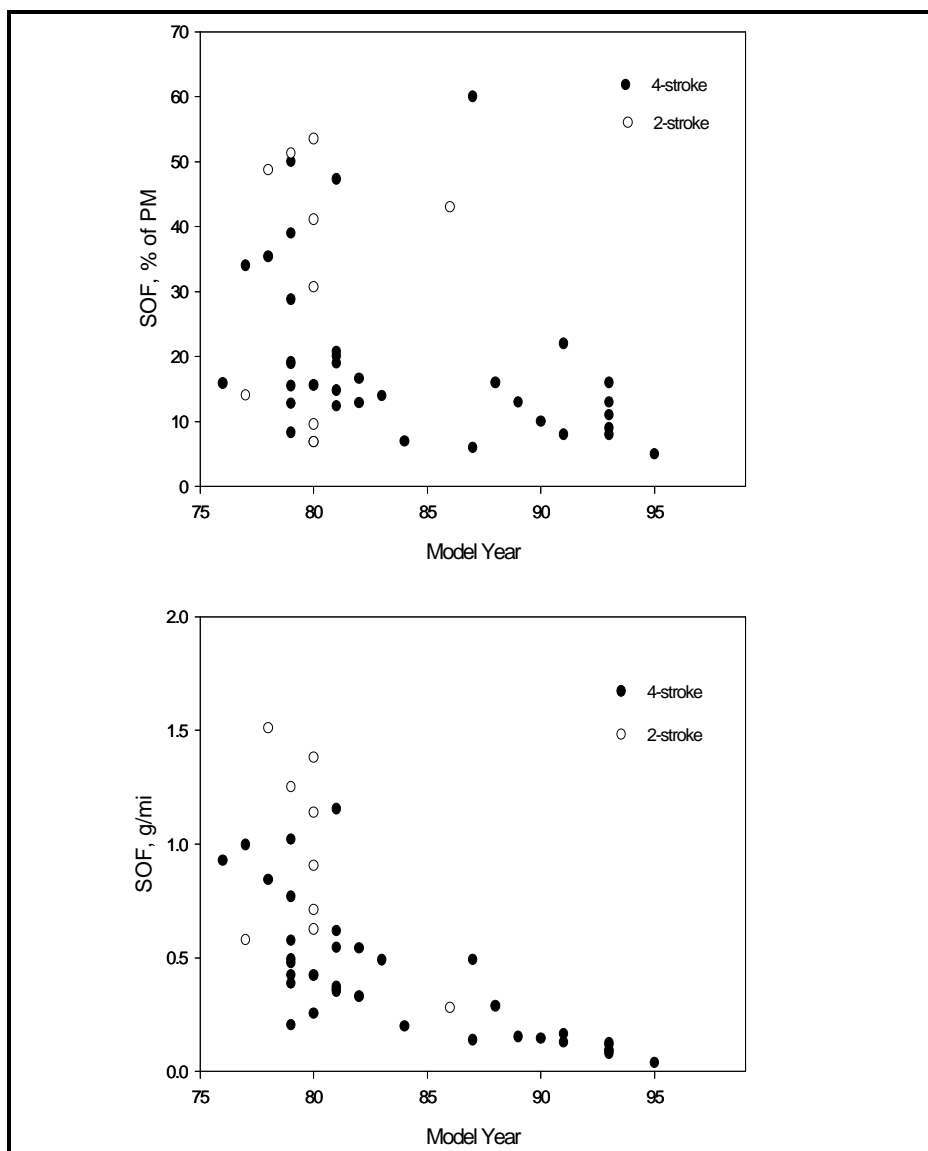


Figure 2-19. Comparison of SOF emissions for 2- and 4-stroke engines in g/mi and as a percentage of total PM.

Sources: Warner-Selph et al., 1984; Dietzmann et al., 1980; Graboski et al., 1998b.

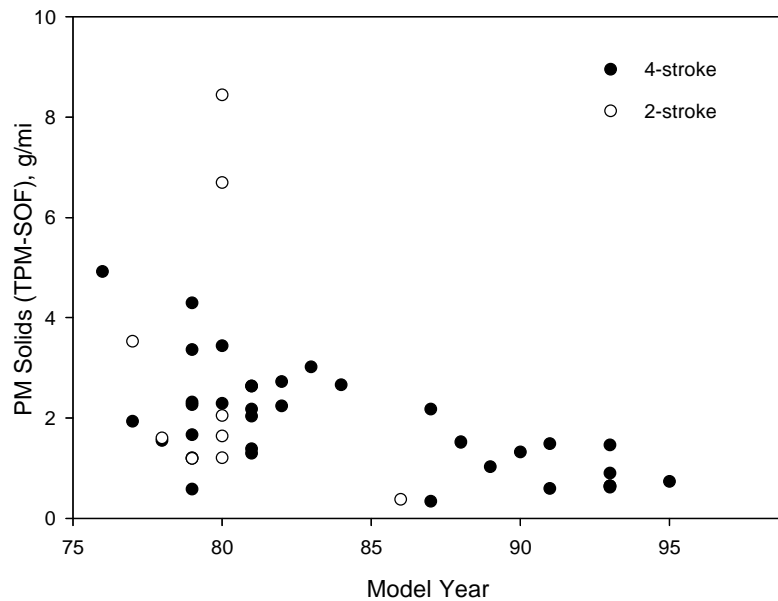


Figure 2-20. Trends in PM solids emissions with model year, a reasonable surrogate for elemental carbon content.

Sources: Yanowitz et al., 1999a; Warner-Selph and Dietzmann, 1984; Dietzmann et al., 1980; Rogge et al., 1993.

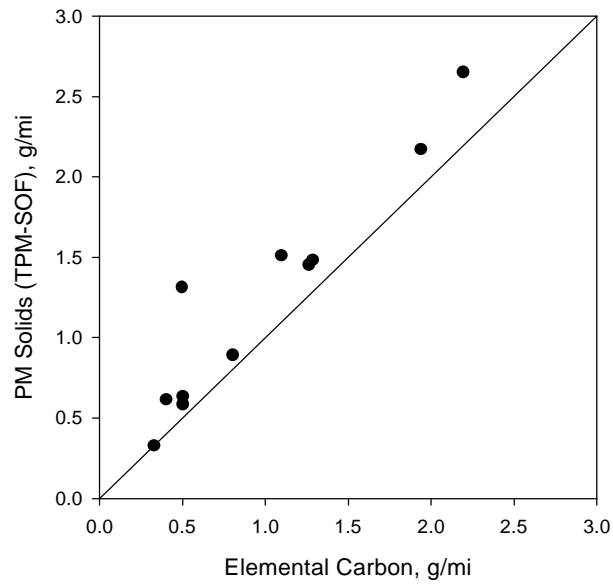


Figure 2-21. Parity plot showing approximate agreement between PM elemental carbon and PM solids measurements in g/mi.
Sources: Yanowitz et al., 1999a; Zielinska et al., 1998.

2.2.6.2. PAHs and Nitro-PAH Emissions

PAHs, nitro-PAHs, and oxidized derivatives of these compounds have attracted considerable attention because of their known mutagenic and, in some cases, carcinogenic character. Nitrated polycyclic aromatic compounds have caused lung cancer and remote metastases in laboratory animals (HEI, 1995). 1-Nitropyrene has been speculated to be the major source of mutagenicity in diesel soot (Noorkhoek and Bos, 1995); however, a large number of other nitro-PAHs are present (Paputa-Peck et al., 1983) and other studies suggest that it is the oxygenated nitro-PAH species that are responsible (Schuetzle et al., 1981; Schuetzle et al., 1985; Ciccioli et al., 1986). For example, Grosovsky and co-workers (1999) have shown that 2-nitrodibenzopyranone (2NDBP) is highly mutagenic in human cells. 3-Nitrobenzanthrone has been shown to be one of the most potent bacterial mutagens known (Enya et al., 1997). 3-Nitrobenzanthrone is also known to be a component of diesel PM, while 2NDBP is proposed to be an atmospheric transformation product of phenanthrene, but may also be present in diesel exhaust.

A few engine and chassis studies have measured PAH emissions. Dietzmann and co-workers (1980) examined four vehicles equipped with late 1970s turbocharged DI engines. Emissions of benzo(a)pyrene from particle extracts were reported and ranged from 1.5 to 9 µg/mi. No gas-phase PAH measurements were reported. No correlation with engine technology (one of the engines was 2-stroke) was observed. Table 2-7 gives the approximate concentrations of several of the abundant nitro-PAHs quantified in early 1980s LD-diesel particulate extracts (with the exception of 3-nitrobenzanthrone, reported recently), in µg/g of particles. Concentrations for some of the nitro-PAHs identified range from 0.3 µg/g for 1,3-dinitropyrene to 8.6 µg/g for 2,7-dinitro-9-fluorenone and 75 µg/g for 1-nitropyrene. More recent nitro-PAH and PAH data for HD diesel engines are reported in units of g/hgp-hr or mass/volume of exhaust, making it impossible to compare them to the older data (Norbeck et al., 1998; Bagley et al., 1996, 1998; Baumgard and Johnson, 1992; Opris et al., 1993; Hansen et al., 1994; Harvey et al., 1994; Kantola et al., 1992; Kreso et al., 1998b; McClure et al., 1992; Pataky et al., 1994).

Rogge and co-workers (1993) reported PAH emissions from particle extracts for two 1987 model year trucks (averaged together, 4-stroke and turbocharged engines). They report results for many specific PAH compounds with total PAHs summing to 0.43 mg/mi and benzo(a)pyrene emissions of 2.7 µg/mi. Particle-phase PAH was about 0.5% of total PM mass. Schauer and co-workers (1999) have recently reported gas- and particle-phase PAH emissions for a 1995 medium-duty turbocharged and intercooled truck. They also report results for a large number of individual PAHs, but summed emissions were 6.9 mg/mi (gas phase) and 1.9 mg/mi (particle phase). Particle-phase PAHs were about 0.7% of total PM mass. Emissions of benzo(a)pyrene were not reported, but emissions of individual species of similar molecular

Table 2-7. Concentrations of nitro-polycyclic aromatic hydrocarbons identified in a LD diesel particulate extract

Nitro-PAH^a	Concentration (µg/g of particles)
4-nitrobiphenyl	2.2
2-nitrofluorene	~1.8
2-nitroanthracene	4.4
9-nitroanthracene	1.2
9-nitrophenanthrene	1.0
3-nitrophenanthrene	4.1
2-methyl-1-nitroanthracene	8.3
1-nitrofluoranthene	1.8
7-nitrofluoranthene	0.7
3-nitrofluoranthene	4.4
8-nitrofluoranthene	0.8
1-nitropyrene	18.9; 75 ^b
6-nitrobenzo[a]pyrene	2.5
1,3-dinitropyrene ^b	0.30
1,6-dinitropyrene ^b	0.40
1,8-dinitropyrene ^b	0.53
2,7-dinitrofluorene ^c	4.2; 6.0
2,7-dinitro-9-fluorenone ^c	8.6; 3.0
3-nitrobenzanthrone ^d	0.6 to 6.6

^aFrom Campbell and Lee (1984) unless noted otherwise. Concentrations recalculated from µg/g of extract to µg/g of particles using a value of 44% for extractable material (w/w).

^bFrom Paputa-Peck et al, 1983.

^cFrom Schuetzle, 1983.

^dFrom Enya et al., 1997 (Isuzu Model 6HEL 7127cc).

weight were approximately 10 µg/mi. Measurements of particle- and gas-phase PAHs conducted for the Northern Front Range Air Quality Study (Zielinska et al., 1998) found the benzo(a)pyrene emission rate to average 13 µg/mi for 15 vehicles ranging from 1983-1993 model years. Summing of individual PAH emissions from this study yields a total PAH rate (combined gas and particle phase) of 13.5 mg/mi.

Benzo(a)pyrene emissions were also reported in the engine dynamometer studies of Springer (1979). A comparison of turbocharged and naturally aspirated engines (both about 1 µg/bhp-h), and of DI and IDI engines (both about 0.15 µg/bhp-h) showed no significant effect of these technology changes on emissions of this compound, as shown in Table 2-8. The difference between 1 and 0.15 µg/bhp-h cannot be attributed to specific technology changes. The engines were from different manufacturers. Bagley and co-workers (1998) studied a 1983 model year IDI, naturally aspirated engine and observed emission levels listed in Table 2-8 from particulate matter extracts. These results can be compared to data presented by Mitchell and co-workers (1994) for two DI turbocharged engines. It is likely that there are also other differences in technology between the 1983 and 1991 engines; however, it is clear that total PM emissions are substantially lower for the newer engines. Results for SOF are inconclusive. Total PAH emissions are the same for the 1983 and 1991 engines and range from 0.05% to 0.15% of the total PM mass. 1-Nitropyrene emissions are near to detection limits and thus the apparent differences are probably not significant.

On the basis of these limited data it is difficult to draw a precise, quantitative conclusion regarding how PAH emissions have changed over time. However, it seems likely that total PAH emissions have been in the range from 0.1 to 15 mg/mi from the early 1970s to the early 1990s. PM-associated PAHs make up on the order of 0.1% of PM mass. Emissions of benzo(a)pyrene were on the order of 10 µg/mi. It is also highly likely that PAH emissions have declined in parallel with emissions of total PM and SOF, which have declined by a factor of approximately 6 over this time period. There is no evidence for a change in PAH emissions out of proportion to the observed changes in mass emissions of PM or SOF.

One chassis study has reported emissions of 1-nitropyrene in PM extracts from 17 HD diesel vehicles (Warner-Selph and Dietzmann, 1984). All engines were turbocharged and direct injected. Results are shown in Figure 2-22; unfortunately there are no distinct trends in these data and the data do not extend to the period of strict emission regulations in the late 1980s. The results suggest, however, that the introduction of new technologies, which did occur to some extent over the model years covered, has not produced dramatic changes in emissions of 1-nitropyrene. Again, it seems likely that nitro-PAH emissions have declined in parallel with decreasing emissions of total PM and SOF.

Table 2-8. Comparison of PAH and nitro-PAH emissions for IDI naturally aspirated engines and two DI turbocharged engines

Emissions, µg/bhp-h	1977 Mack ETAY(B)673A DI, turbo- charged, aftercooled	1977 Caterpillar 3206, DI, turbocharged, aftercooled	1977 Caterpillar 3206, IDI, turbocharged, aftercooled	1977 Daimler- Benz OM- 352A, DI, turbo- charged, aftercooled	1977 Daimler- Benz OM- 352A, DI, naturally aspirated	1983 Caterpillar 3304 IDI, naturally aspirated	1991 DDC Series 60 DI, turbocharged, aftercooled	1991 Navistar DTA466, DI, turbocharged, aftercooled
PM (g/bhp-h)	0.61	.35	0.28	0.56	0.99	0.56	0.12	0.1
SOF (%)	16	18	11	34	29	57	26	55
PAH	--	--	--	--	--	132.5	131	145
Benzopyrene	2.23	0.15	0.10	0.87	1.07	1.5	--	0.05
Nitro-PAH	--	--	--	--	--	--	0.18	0.65
1-Nitro- pyrene	--	--	--	--	--	2.2	0.06	0.32

Sources: Springer, 1979; Bagley et al., 1998; Mitchell et al., 1994.

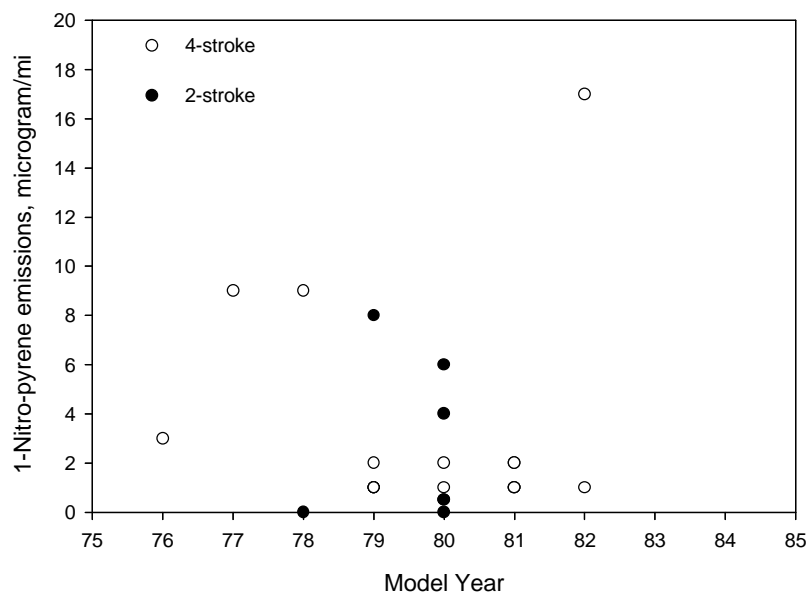


Figure 2-22. 1-Nitropyrene emission rates from several HD diesel vehicles.
Source: Warner-Selph et al., 1984.

2.2.6.3. *Aldehyde Emissions*

Many aldehydes of interest typically occur in the gas phase rather than the particle phase of diesel exhaust. Some aldehydes are also known carcinogens and there are considerable data on aldehyde emissions from diesel engines. Figure 2-23 reports mg/mile total aldehyde emissions from chassis dynamometer studies (Warner-Selph and Dietzmann, 1984; Schauer et al., 1999; Unnasch et al., 1993). The results indicate no difference between 2 and 4-stroke engines, although aldehyde emissions appear to have declined substantially since 1980 on the basis of a limited number of data points (only 2). Engine dynamometer studies show aldehyde emission levels of 150-300 mg/bhp-h for late 1970s engines with no significant effect of turbocharging, or IDI versus DI. High-pressure fuel injection may have resulted in a marginal increase in aldehyde emissions (Springer, 1979). By comparison, 1991 model year engines (DI, turbocharged) exhibited aldehyde emissions in the 30-50 mg/bhp-h range (Mitchell et al., 1994). It seems likely that aldehyde emissions have declined by perhaps one order of magnitude since about 1980, on average, in line with the decline in total PM and SOF emissions. Insufficient information is available to determine the cause of this decline; however, more complete combustion because of higher pressure fuel injection coupled with leaner operation because of turbocharging with aftercooling is the most likely cause.

2.2.6.4. *Dioxin and Furan Emissions*

Dioxin and furan emissions from on-road HD diesel vehicles were measured in the Fort McHenry Tunnel in Baltimore, MD (Gertler et al., 1998). For the limited range of vehicle operating conditions in the tunnel, the average HD diesel emission factor was 0.28 ± 0.13 ng-TEQ/mi. This is a factor of 3 lower than the initial EPA estimate (Gertler et al., 1998). The recent dynamometer measurements from a HD diesel engine (Cummins L10) showed negligible dioxin and furan emission rates (Norbeck et al., 1998).

2.2.6.5. *Particle Size*

Figure 2-24 shows the general size distribution for diesel particulate based on mass and particle number. Most of the mass is accumulation mode particles ranging in size from 50 to 700 nm and averaging about 200 nm. Aggregated carbonaceous particles and absorbed organic material are primarily in this mode. The nuclei mode consists of particles in the 5-50 nm range, averaging about 20 nm. These are believed to form from exhaust constituents during cooling and to consist of sulfuric acid droplets, ash particles, condensed organic material, and perhaps primary carbon spherules (Abdul-Khalek et al., 1998; Baumgard and Johnson, 1996). The nuclei mode typically contains from 1%-20% of particle mass and from 50%-90% of the particle number.

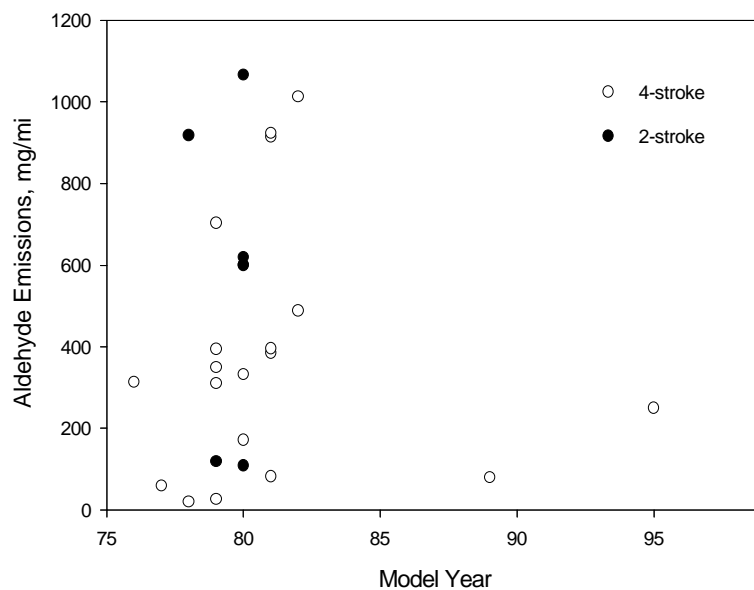


Figure 2-23. Chassis dynamometer measurements of total aldehyde emissions from HD diesel vehicles.

Sources: Warner-Selph and Dietzmann, 1984; Schauer et al., 1999; Unnasch et al., 1993.

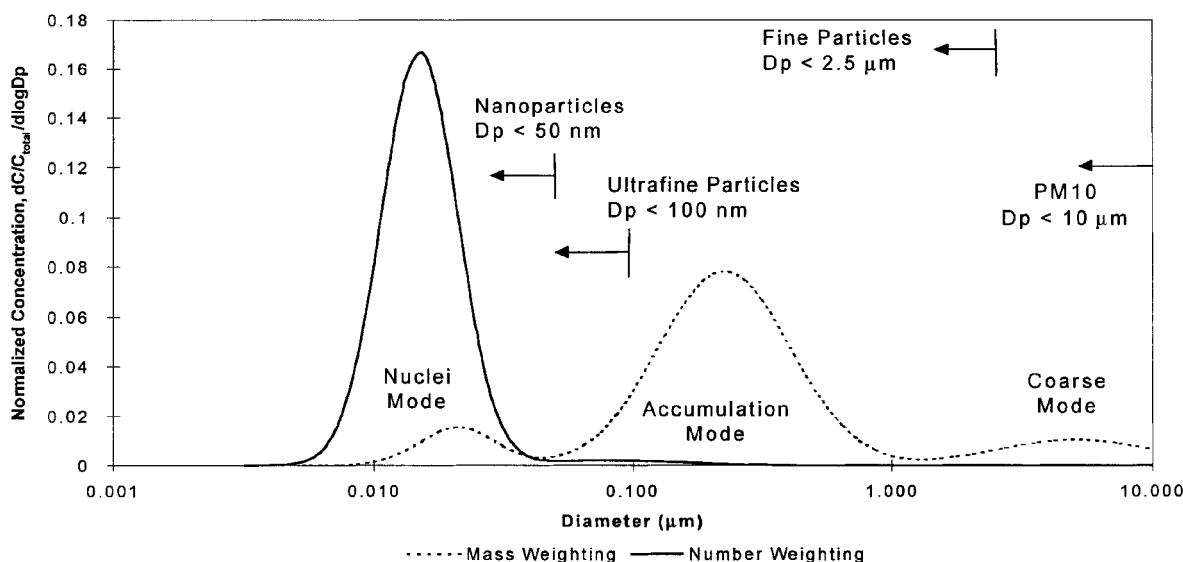


Figure 2-24. Particle size distribution in diesel exhaust, taken from Kittelson (1998).

Measurements made on diluted diesel exhaust typically show higher numbers of nuclei-mode particles than do measurements made on raw exhaust because of condensation to form nuclei mode aerosol upon cooling of the exhaust. Dilution ratio, sampling temperature, and other sampling factors can therefore have a large impact on the number and makeup of nuclei mode particles (Abdul-Khalek et al., 1999). Just as diesel exhaust particulate matter is defined by how it is collected (i.e., on a filter at or below 52 °C); the size distribution of diesel exhaust is also determined by how it is measured. Baumgard and Johnson (1996) have proposed that accumulation-mode particles are formed in the combustion chamber whereas nuclei-mode particles are formed during the dilution and measurement process. It seems likely that the situation is not nearly so clear-cut and that both accumulation and nuclei-mode particles are formed in the combustion chamber, but that a large number of additional nuclei-mode particles are formed during dilution.

Several groups have shown that decreasing sulfur content decreases the number of nuclei-mode particles measured in the exhaust, assuming temperature is low enough and residence time is long enough for nucleation and condensation of sulfate aerosol and water (Baumgard and Johnson, 1992; Opris et al., 1993; Baumgard and Johnson, 1996; Abdul-Khalek et al., 1999).

1 The application of this finding to real-world conditions is difficult to predict, as the number of
2 nuclei-mode particles formed from sulfate and water in the atmosphere will be determined by
3 atmospheric conditions, not by dilution tunnel conditions.

4 More controversial is the suggestion that PM emission size distribution from newer
5 technology engines (1991 and later) may be shifted to have a much higher number concentration
6 of nuclei-mode particles, independent of fuel sulfur content (Kreso et al., 1998b; Abdul-Khalek
7 et al., 1998; Baumgard and Johnson, 1996; Bagley et al., 1996). For example, in the study of
8 Kreso and coworkers (1998b), a comparison of emissions from a 1995 model year engine
9 measured in that work with measurements made on 1991 (Bagley et al., 1996) and 1988 (Bagley
10 et al., 1993) model year engines in earlier studies is presented. Dilution conditions (relatively low
11 temperature, low primary dilution ratio, long residence time of more than 3 seconds) strongly
12 favor the formation of nucleation products. The 1991 and 1988 engines were tested with 100
13 ppm sulfur fuel while the 1995 engine was tested with 310 ppm sulfur fuel, which may confound
14 the results to some extent. Nuclei-mode particles made up 40% to 60% of the number fraction of
15 PM emissions for the 1988 engine and 97%+ of the PM from the 1991 and 1995 engines.
16 Number concentrations were also roughly two orders of magnitude higher for the newer engines.
17 SOF made up 25%-30% of PM in the 1988 engine and 40%-80% of PM for the newer engines.
18 Total PM was significantly reduced for the newer engines. It was suggested that increased fuel
19 injection pressure leads to improved fuel atomization and evaporation, leading to smaller primary
20 carbonaceous particles, but there appears to be no more direct experimental or computational
21 evidence supporting this hypothesis. The high degree of SOF with the 1991 engine, particularly
22 at high-load test modes, was also inconsistent with measured SOF values of other engines using
23 similar types of technology (Last et al., 1995, Ullman et al., 1995). Kittelson (1998) notes that
24 there is far less soot-type particulate and that higher number concentrations of the small particles
25 are formed from nucleation of VOC and sulfuric acid-type compounds.

26 At present, no conclusions can be made regarding the reported shift in size distribution
27 because:

- 28
29 • The result may simply be a sampling artifact because of the substantial effect of
30 dilution conditions on measured particle size distributions. The results may also be a
31 sampling artifact because no study has reported back-to-back testing of engines with
32 varying technology. All results are based on a comparison of results from individual
33 studies performed over several years. Only recently has the impact of sampling
34 conditions begun to be understood, and thus early results, and results that are not
35 clearly obtained under identical sampling conditions, may lead to erroneous
36 conclusions. Extensive research is underway to understand the factors in the

sampling procedure that affect the PM size distribution and to determine the actual size distribution (Kittelson et al., 1999).

- The result may not be relevant to the fate of engine exhaust in the atmosphere. It is unclear what sampling conditions are appropriate for these studies. If understanding the fate of the exhaust in the atmosphere is the intended use of the study, then simulation of atmospheric dilution conditions is desirable. On the other hand, some studies may be more interested in the impact of engine technology on engine emissions with no sampling artifacts. Given an understanding of the atmospheric chemistry and physics, engine emissions might also be used to predict the formation of aerosol in the atmosphere. An understanding of these factors can only come through knowledge of the chemical composition of nuclei-mode particles and through studies of the fate of diesel exhaust in the atmosphere (an alarmingly complex situation).
- Particle sizing studies have been performed under steady-state conditions that are probably not representative of how nearly all diesel particulate is actually formed in use. Engine transients create temporary situations that favor PM production, and in all likelihood more than 90% of diesel PM in use is generated under these conditions.

2.3. ATMOSPHERIC TRANSFORMATION OF DIESEL EXHAUST

Primary diesel emissions are a complex mixture containing hundreds of organic and inorganic constituents in the gas and particle phases, the most abundant of which are listed in Table 2-9. The more reactive compounds with short atmospheric lifetimes will undergo rapid transformation in the presence of the appropriate reactants, whereas more stable pollutants can be transported over greater distances. A knowledge of the atmospheric transformations of gaseous and particulate components of diesel emissions and their fate is important in assessing environmental exposures and risks. This section describes some of the major atmospheric transformation processes for gas-phase and particle-phase diesel exhaust, focusing on the primary and secondary organic compounds that are of significance for human health. For a more comprehensive summary of the atmospheric transport and transformation of diesel emissions see Winer and Busby (1995).

Table 2-9. Classes of compounds in diesel exhaust

Particulate phase		Gas phase	
Heterocyclics, hydrocarbons (C ₁₄ -C ₃₅), and PAHs and derivatives:		Heterocyclics, hydrocarbons (C ₁ -C ₁₀), and derivatives:	
Acids	Cycloalkanes	Acids	Cycloalkanes, Cycloalkenes
Alcohols	Esters	Aldehydes	Dicarbonyls
Alkanoic acids	Halogenated cmpds.	Alkanoic acids	Ethyne
n-Alkanes	Ketones	n-Alkanes	Halogenated cmpds.
Anhydrides	Nitrated cmpds.	n-Alkenes	Ketones
Aromatic acids	Sulfonates	Anhydrides	Nitrated cmpds.
	Quinones	Aromatic acids	Sulfonates
			Quinones
Elemental carbon		Acrolein	
Inorganic sulfates and nitrates		Ammonia	
Metals		Carbon dioxide, carbon monoxide	
Water		Benzene	
		1,3-Butadiene	
		Formaldehyde	
		Formic acid	
		Hydrogen cyanide, hydrogen sulfide	
		Methane, methanol	
		Nitric and nitrous acids	
		Nitrogen oxides, nitrous oxide	
		Sulfur dioxide	
		Toluene	
		Water	

Source: Mauderly (1992), which summarized the work of Lies et al., 1986; Schuetzle and Frazier, 1986; Carey 1987; Zaebs et al., 1988; updated from recent work by Johnson, 1993; McDonald, 1997; Schauer et al., 1999.

2.3.1. Gas-Phase Diesel Exhaust

Gas-phase diesel exhaust contains of several organic and inorganic compounds which undergo various chemical and physical transformations in the atmosphere depending on the abundance of reactants and meteorological factors such as wind speed and direction, solar irradiance, humidity, temperature, and precipitation. Gaseous diesel exhaust will primarily react with the following species (Atkinson, 1988):

- Sunlight, during daylight hours;
- Hydroxyl radical (OH), during daylight hours;
- Ozone (O₃), during daytime and nighttime;
- Hydroperoxyl radical HO₂, typically during afternoon/evening hours;
- Gaseous nitrate radicals (NO₃) or dinitrogen pentoxide (N₂O₅), during nighttime hours; and
- Gaseous nitric acid (HNO₃) and other species such as nitrous acid (HONO) and sulfuric acid (H₂SO₄).

1 The major loss process for most of the diesel exhaust emission constituents is oxidation,
2 which occurs primarily by daytime reaction with OH radical (Table 2-10). For some pollutants,
3 photolysis, reaction with ozone, and reactions with NO₃ radicals during nighttime hours are also
4 important removal processes. The atmospheric lifetimes do not take into consideration the
5 potential chemical or biological importance of the products of these various reactions. For
6 example, the reaction of gas-phase PAHs with NO₃ appears to be of minor significance as a PAH
7 loss process, but is more important as a route of formation of mutagenic nitro-PAHs. The
8 reaction products for some of the major gaseous diesel exhaust compounds are listed in Table 2-
9 11 and are discussed briefly below.

10 11 **2.3.1.1. Organic Compounds**

12 The organic fraction of diesel exhaust is a complex mixture of compounds, very few of
13 which have been characterized. The atmospheric chemistry of several organic constituents of
14 diesel exhaust (which are also produced by other combustion sources) has been studied. A few of
15 these reactions and their products are discussed below. For a complete summary of the
16 atmospheric chemistry of organic combustion products, see Seinfeld and Pandis (1998).

17 Acetaldehyde forms peroxyacetyl nitrate (PAN), which has been shown to be a direct-
18 acting mutagen toward *S. typhimurium* strain TA100 (Kleindienst et al., 1985) and is phytotoxic.
19 Benzaldehyde, the simplest aromatic aldehyde, forms peroxybenzoyl nitrate or nitrophenols
20 following reaction with oxides of nitrogen (Table 2-11).

21 For those PAHs present in the gas phase, reaction with the hydroxyl radical is the major
22 removal route, leading to atmospheric lifetimes of a few hours. The gas-phase reaction of PAHs
23 containing a cyclopenta-fused ring, such as acenaphthene, acenaphthylene, and acephenanthrylene
24 with the nitrate radical may be an important loss process during nighttime hours. Relatively few
25 data are available concerning the products of these gas-phase reactions. It has been shown that,
26 in the presence of NO_x, the OH radical reactions with naphthalene, 1- and 2-methylnaphthalene,
27 acenaphthylene, biphenyl, fluoranthene, pyrene, and acephenanthrylene lead to the formation of
28 nitroarenes (Arey et al., 1986; Atkinson et al., 1986; 1990; Zielinska et al., 1988; 1989a; Arey,
29 1998). In addition, in a 2-step process involving OH radical reaction and NO₂ addition, 2-
30 nitrofluoranthene and 2-nitropyrene can be formed and eventually partition to the particle phase,
31 as will other nitro-PAHs.

32 The addition of the NO₃ radical to the PAH aromatic ring leads to nitroarene formation
33 (Sweetman et al., 1986; Atkinson et al., 1987, 1990; Zielinska et al., 1989a). The gas-phase
34 reactions of NO₃ radical with naphthalene, 1- and 2-methylnaphthalene, acenaphthene,
35 phenanthrene, anthracene, fluoranthene, and pyrene produce, in general, the same nitro-PAH
36 isomers as the OH radical reaction, but with different yields (Arey et al., 1989; Sweetman et al.,

Table 2-10. Calculated atmospheric lifetimes for gas-phase reactions of selected compounds present in automotive emissions with important reactive species

Compound	Atmospheric lifetime resulting from reaction with:				
	OH ^a	O ₃ ^b	NO ₃ ^c	HO ₂ ^d	hν ^e
NO ₂	1.3 days	12 h	24 min	2 h	2 min
NO	2.5 days	1 min	1.2 min	20 min	-
HNO ₃	110 days	-	-	-	-
SO ₂	16 days	>200 years	>1.4×10 ⁴ years	>600 years	-
NH ₃	90 days	-	-	-	-
Propane	12 days	>7000 years	-	-	-
n-Butane	5.6 days	>4500 years	3.6 years	-	-
n-Octane	1.9 days	-	1.2 years	-	-
Ethylene	1.9 days	9 days	1.2 years	-	-
Propylene	7 h	1.5 days	6 days	-	-
Acetylene	19 days	6 years	>5.6 years	-	-
Formaldehyde	1.9 days	>2 - 104 years	84 days	23 days	4 h
Acetaldehyde	0.6 day	>7 years	20 days	-	60 h
Benzaldehyde	1.2 days	-	24 days	-	-
Acrolein	0.6 day	60 days	-	-	-
Formic acid	31 days	-	-	-	-
Benzene	11 days	600 years	>6.4 years	-	-
Toluene	2.5 days	300 years	3.6 years	-	-
m-Xylene	7 h	75 years	0.8 years	-	-
Phenol	6 h	-	8 min	-	-
Naphthalene ^f	6.8 h	>80 days	1.5 years	-	-
2-Methylnaphthalene ^f	2.8 h	>40 days	180 days		-
1-Nitronaphthalene ^f	2.3 days	>28 days	1 8 years		1.7 h
Acenaphthene ^f	1.5 h	>30 days	1.2 h	-	-
Acenaphthylene ^f	1.3 h	~43 min	6 min	-	-
Phenanthrene ^f	11.2 h	41 days	4.6 h	-	-
Anthracene ^f	8.6 h	-	-	-	-
Fluoranthene ^f	~2.9 h	-	~1 year	-	-
Pyrene ^f	~2.9 h	-	~ 120 days	-	-

^a For 12-h average concentration of OH radical of 1.6×10⁶ molecule/cm³ (Prinn et al., 1992).

^b For 24-h average O₃ concentration of 7×10¹¹ molecule/cm³.

^c For 12-h average NO₃ concentration of 5×10⁸ molecule/cm³ (Atkinson, 1991).

^d For 12-h average HO₂ concentration of 10⁸ molecule/cm³.

^e For solar zenith angle of 0°.

^f Lifetimes from Arey (1998), for 12-h concentration of OH radical of 1.9×10⁶ molecule/cm³.

Source: Winer and Busby (1995) unless noted otherwise.

Table 2-11. Major components of gas-phase diesel engine emissions and their known atmospheric transformation products

Emission component	Atmospheric reaction products
Carbon dioxide	————
Carbon monoxide	————
Oxides of nitrogen	Nitric acid, ozone
Sulfur dioxide	Sulfuric acid
Hydrocarbons:	
Alkanes ($\leq C_{18}$)	Aldehydes, alkyl nitrates, ketones
Alkenes ($\leq C_4$) (e.g., 1,3-butadiene)	Aldehydes, ketones
Aldehydes:	
Formaldehyde	Carbon monoxide, hydroperoxyl radicals
Higher aldehydes (e.g., acetaldehyde, acrolein)	Peroxyacyl nitrates
Monocyclic aromatic compounds (e.g., benzene, toluene)	Hydroxylated and hydroxylated-nitro derivatives ^a
PAHs (≤ 4 rings) (e.g., phenanthrene, fluoranthene) ^b	Nitro-PAHs (4 rings) ^c
Nitro-PAHs (2 and 3 rings) (e.g., nitronaphthalenes)	Quinones and hydroxylated-nitro derivatives

^a Some reaction products expected to partition into the particle phase.

^b Nitro-PAHs with more than two rings will partition into the particle phase.

^c PAHs containing four rings are usually present in both the vapor and particle phases.

Source: Adapted from Winer and Busby, 1995.

1986; Atkinson et al., 1987, 1990; Zielinska et al., 1986, 1989a). For example, the same 2-NF is produced from both OH radical and NO₃ gas-phase reactions, but the reaction with NO₃ produces a much higher yield. While the production of several nitroarene compounds has been studied in environmental chambers (Arey et al., 1989; Zielinska et al., 1990; Atkinson and Arey, 1994; Arey, 1998; Feilberg et al., 1999), generally the same nitro-PAH isomers formed from reaction with OH and NO₃ radicals are observed in ambient air samples. Secondary formation of nitroarenes through the gas-phase reactions of the 2-, 3-, and 4-ring PAHs is the major source for many of the nitroarenes observed in ambient air (Pitts et al., 1985a,b,c; Arey et al., 1986; Zielinska et al., 1988). Photolysis is the major removal pathway for nitroarenes with lifetimes of approximately 2 hours (Feilberg et al., 1999; Nielsen and Ramdahl, 1986).

2.3.1.2. Inorganic Compounds

Sulfur dioxide (SO₂) and oxides of nitrogen (primarily NO) are emitted from diesel engines. Sulfur dioxide is readily oxidized by the OH radical in the atmosphere, followed by formation of the HO₂ radical and HSO₃, which rapidly reacts with water to form sulfuric acid (H₂SO₄) aerosols. Because SO₂ is soluble in water, it is scavenged by fog, cloud water, and raindrops. In aqueous systems, SO₂ is readily oxidized to sulfate by reaction with H₂O₂, O₃, or O₂ in the presence of a

metal catalyst (Calvert and Stockwell, 1983). Sulfur emitted from diesel engines is predominantly (~98%) in the form of SO₂, a portion of which will form sulfate aerosols by the reaction described above. Off-road equipment, which typically uses fuel containing 3300 ppm sulfate, emits more SO₂ than on-road diesel engines, which use fuels currently containing an average of 340 ppm sulfur because of EPA regulations effective in 1993 decreasing diesel fuel sulfur levels. EPA (1998b) estimates that mobile sources are responsible for about 7% of nationwide SO₂ emissions, with diesel engines contributing 80% of the mobile source total (the majority of the diesel SO₂ emissions originate from nonroad engines) (U.S. EPA, 1998b).

Nitric oxide (NO) is also oxidized in the atmosphere to form NO₂ and particulate nitrate. The fraction of motor vehicle NO_x exhaust converted to particulate nitrate in a 24-hour period has been calculated using a box model to be approximately 3.5% nationwide, a portion of which can be attributed to diesel exhaust (Gray and Kuklin, 1996). EPA estimates that in 1997, mobile sources were responsible for about 50% of nationwide NO_x emissions, with diesel engines being responsible for approximately half of the mobile source total (U.S. EPA, 1998b).

2.3.1.3. Atmospheric Transport of Gas-Phase Diesel Exhaust

Gas-phase diesel exhaust can be dry deposited, depending on the deposition surface, atmospheric stability, and the solubility and other chemical properties of the compound. Dry deposition of organic species is typically on the order of weeks to months, with dry deposition velocities of approximately 10⁻⁴ cm/sec (Winer and Busby, 1995). In contrast, inorganic species such as sulfur dioxide and nitric acid have relatively fast deposition rates (0.1-2.5 cm/sec) and will remain in the atmosphere for shorter time periods compared with the organic exhaust components. Some gas-phase species will also be scavenged by aqueous aerosols and potentially deposited via precipitation. These processes can greatly reduce the atmospheric concentration of some vapor-phase species. Atmospheric lifetimes for several gas-phase components of diesel exhaust are on the order of hours or days, during which time atmospheric turbulence and advection can disperse these pollutants widely.

2.3.2. Particle-Phase Diesel Exhaust

Particle-associated diesel exhaust is composed of primarily carbonaceous material (organic and elemental carbon) with a very small fraction composed of inorganic compounds and metals. The organic carbon fraction adsorbed on diesel PM is composed of high-molecular-weight compounds, such as PAHs, which are generally more resistant to atmospheric reactions than PAHs in the gas phase. The elemental carbon component of diesel exhaust is inert to atmospheric degradation, while the PAH compounds are degraded by reaction with the following species:

- Sunlight, during daylight hours;

- Ozone (O₃), during daytime and nighttime;
- Nitrate radical (NO₃) and dinitrogen pentoxide (N₂O₅), during nighttime hours;
- Hydroxyl (OH) and hydroperoxyl radicals (HO₂);
- NO₂, during nighttime and daytime hours;
- Hydrogen peroxide (H₂O₂); and
- Gaseous nitric acid (HNO₃) and other species such as nitrous acid (HONO) and sulfuric acid (H₂SO₄).

Since many of the PAH derivatives formed by reaction with some of the reactants listed above have been found to be highly mutagenic, a brief discussion of PAH photolysis, nitration, and oxidation follows. Some of the major degradation products from particulate diesel exhaust are listed in Table 2-12.

Table 2-12. Major components of particle-phase diesel engine emissions and their known atmospheric transformation products

Emission component	Atmospheric reaction products
Elemental carbon	_____
Inorganic sulfate	_____
Hydrocarbons (C ₁₄ -C ₃₅)	Little information; possibly aldehydes, ketones, and alkyl nitrates
PAHs (≥4 rings) (e.g., pyrene, benzo[a]pyrene)	Nitro-PAHs (≥4 rings); Nitro-PAH lactones
Nitro-PAHs (≥3 rings) (e.g., nitropyrenes)	Hydroxylated-nitro derivatives

Source: Adapted from Winer and Busby, 1995.

2.3.2.1. Particle-Associated PAH Photooxidation

Laboratory studies of photolysis of PAHs adsorbed on 18 different fly ashes, carbon black, silica gel, and alumina (Behymer and Hites, 1985, 1988) and several coal stack ashes (Yokely et al., 1986; Dunstan et al., 1989) have shown that the extent of photodegradation of PAHs depends very much on the nature of the substrate to which they are adsorbed. The dominant factor in the stabilization of PAHs adsorbed on fly ash was the color of the fly ash, which is related to the

amount of black carbon present. It appears that PAHs were stabilized if the carbon black content of the fly ash was greater than approximately 5%. On black substrates, half-lives of PAHs studied were on the order of several days (Behymer and Hites, 1988).

The environmental chamber studies of Kamens et al. (1988) on the daytime decay of PAHs present on residential wood smoke particles and on gasoline internal combustion emission particles showed PAH half-lives of approximately 1 hour at moderate humidities and temperatures. At very low-angle sunlight, very low water-vapor concentration, or very low temperatures, PAH daytime half-lives increased to a period of days. The presence and composition of an organic layer on the aerosol seems to influence the rate of PAH photolysis (Jang and McDow, 1995; McDow et al., 1994; Odum et al., 1994).

Because of limited understanding of the mechanisms of these complex heterogeneous reactions, it is currently impossible to draw any firm conclusion concerning the photostability of particle-bound PAHs in the atmosphere. Because diesel particulate matter contains a relatively high quantity of elemental carbon, it is reasonable to speculate that PAHs adsorbed onto these particles might be relatively stable under standard atmospheric conditions, leading to an anticipated half-life of 1 or more days.

2.3.2.2. Particle-Associated PAH Nitration

Since 1978, when Pitts et al. (1978) first demonstrated that benzo(a)pyrene deposited on glass-fiber filters exposed to air containing 0.25 ppm NO₂ with traces of HNO₃ formed nitro-benzo(a)pyrene, numerous studies of the heterogeneous nitration reactions of PAHs adsorbed on a variety of substrates in different simulated atmospheres have been carried out (Finlayson-Pitts and Pitts, 1986). PAHs deposited on glass-fiber and Teflon-impregnated glass-fiber filters react with gaseous N₂O₅, yielding their nitro derivatives (Pitts et al., 1985b,c). The most abundant isomers formed were 1-nitropyrene (1-NP) from pyrene, 6-nitro-benzo(a)pyrene from benzo(a)pyrene, and 3-nitroperylene from perylene.

The formation of nitro-PAHs during sampling may be an important consideration for diesel PM collection because of the presence of NO₂ and HNO₃ (Feilberg et al., 1999). However, Schuetzle (1983) concluded that the artifact formation of 1-NP was less than 10%-20% of the 1-NP present in the diesel particles if the sampling time was less than 23 min (one FTP cycle) and if the sampling temperature was not higher than 43 °C. The formation of nitroarenes during ambient high-volume sampling conditions has been reported to be minimal, at least for the most abundant nitropyrene and nitrofluoranthene isomers (Arey et al., 1988).

Diesel PM contains a variety of nitroarenes, with 1-NP being the most abundant among identified nitro-PAHs. The concentration of 1-NP was measured in the extract of particulate samples collected at the Allegheny Mountain Tunnel on the Pennsylvania Turnpike as 2.1 ppm and ~5 ppm by mass of the extractable material from diesel and SI vehicle PM, respectively.

These values are much lower than would be predicted on the basis of laboratory measurements for either diesel or SI engines (Gorse et al., 1983).

Several nitroarene measurements have been conducted in airsheds heavily affected by motor vehicle emissions (Arey et al., 1987; Atkinson et al., 1988; Zielinska et al., 1989a,b; Ciccioli et al., 1989, 1993). Ambient PM samples were collected at three sites in the Los Angeles Basin during two summertime periods and one wintertime period. Concentrations of 1-NP ranged from 3 pg/m³ to 60 pg/m³ and 3-NF was also present in diesel PM at concentrations ranging from not detectable to 70 pg/m³.

2.3.2.3. Particle-Associated PAH Ozonolysis

Numerous laboratory studies have shown that PAHs deposited on combustion-generated fine particles and on model substrates undergo reaction with O₃ (Katz et al., 1979; Pitts et al., 1980, 1986; Van Vaeck and Van Cauwenberghe, 1984; Finlayson-Pitts and Pitts, 1986). The dark reaction toward O₃ of several PAHs deposited on model substrates has been shown to be relatively fast under simulated atmospheric conditions (Katz et al., 1979; Pitts et al., 1980, 1986). Half-lives on the order of one to several hours were reported for the more reactive PAHs, such as benzo[a]pyrene, anthracene, and benz[a]anthracene (Katz et al., 1979).

The reaction of PAHs deposited on diesel particles with 1.5 ppm O₃ under high-volume sampling conditions has been shown to be relatively fast, and half-lives on the order of 0.5 to 1 hour have been reported for most PAHs studied (Van Vaeck and Van Cauwenberghe, 1984). The most reactive PAHs include benzo(a)pyrene, perylene, benz[a]anthracene, cyclopenta[cd]pyrene, and benzo[ghi]perylene. The benzo[fluoranthene] isomers are the least reactive of the PAHs studied, and benzo[e]perylene is less reactive than its isomer benzo[a]pyrene. The implications of this study for the high-volume sampling ambient POM are important: reaction of PAHs with O₃ could possibly occur under high-volume sampling conditions during severe photochemical smog episodes, when the ambient level of O₃ is high. However, the magnitude of this artifact is difficult to assess from available data.

2.3.2.4. Atmospheric Transport of Diesel Exhaust Particle Matter

Ultrafine particles emitted by diesel engines undergo nucleation, coagulation, and condensation to form fine particles. PM can be removed from the atmosphere by dry and wet deposition. Particles of small diameter (<1 µm), such as diesel PM, are removed less efficiently than larger particles by wet and dry deposition and thus have longer atmospheric residence times. Dry deposition rates vary depending on the particle size. Because of their small size, diesel exhaust particles will have residence times of several days (dry deposition velocities of approximately 0.01 cm/sec) (Winer and Busby, 1995). Diesel particulates may be removed by

wet deposition if they serve as condensation nuclei for water vapor deposition, or are scavenged by precipitation in- or below-cloud.

In a study designed to assess the atmospheric concentrations and transport of diesel exhaust particles, Horvath et al. (1988) doped the sole source of diesel fuel in Vienna with an organometallic compound of the heavy earth element dysprosium. The authors found that in some of the more remote sampling areas, diesel PM comprised more than 30% of the particulate mass, indicating that diesel PM can be dispersed widely.

2.3.3. Diesel Exhaust Aging

After emission from the tailpipe, diesel exhaust undergoes dilution, reaction, and transport in the atmosphere. The primary emission is considered “fresh,” while “aged” diesel exhaust is considered to have undergone chemical and physical transformation and dispersion over a period of a day or two. Laboratory dilution tunnel measurements represent a homogeneous environment compared to the complex and dynamic system into which real-world diesel exhaust is emitted. The physical and chemical transformation of diesel exhaust will vary depending on the environment into which it is emitted. In an urban or industrial environment, diesel exhaust may enter an atmosphere with high concentrations of oxidizing and nitrating radicals, as well as nondiesel organic and inorganic compounds that may influence the toxicity, chemical stability, and atmospheric residence time. In general, secondary pollutants formed in an aged aerosol mass are more oxidized, and therefore have increased polarity and water solubility (Finlayson-Pitts and Pitts, 1986). These oxidized compounds may be removed at rates different from their precursor compounds and may exhibit different biological reactivities.

In addition, particle size distributions may vary depending on aggregation and coagulation phenomena in the aging process. People in vehicles, near roadways (e.g., cyclists, pedestrians, people in nearby buildings) and on motorcycles will be exposed to more fresh exhaust than the general population. In some settings where emissions are entrained for long periods through meteorological or other factors, exposures would be expected to include both fresh and aged diesel exhaust. The complexities of transport and dispersion of emission arising from motor vehicles have been the subject of extensive modeling and experimental studies over the past decades and have been summarized by Sampson (1988); exposures to diesel PM are discussed in the next section of this chapter.

The major organic constituents of diesel exhaust and their potential degradation pathways described above provide evidence for (1) direct emission of PAHs, (2) formation of nitroarenes, and (3) secondary sulfate and nitrate formation. Since nitro-PAH products are often more mutagenic than their precursors, the formation, transport, and concentrations of these compounds in an aged aerosol mass are of significant interest.

2.4. AMBIENT DIESEL EXHAUST CONCENTRATIONS AND EXPOSURES

2.4.1. Diesel Exhaust Gases in the Ambient Atmosphere

Diesel exhaust gas is a complex mixture composed mainly of nitrogen, carbon dioxide, carbon monoxide, sulfur dioxide, and volatile organic compounds including aldehydes, alkanes, alkenes, and aromatic compounds such as benzene, toluene, 1,3-butadiene, naphthalene, and other low-molecular-weight aromatics. The primary source of these gas-phase compounds is incomplete fuel combustion and lubricating oil, with some contribution from compounds formed during the combustion process or by reaction with catalysts (Johnson et al., 1994). While direct emissions of several diesel exhaust components have been measured, few studies have attempted to elucidate the contribution of diesel-powered engines to atmospheric concentrations of these components, most of which are emitted by several combustion sources.

The emission profile of gaseous organic compounds is different for diesel and SI vehicles; the low-molecular-weight aromatic hydrocarbons and alkanes ($<C_9$) are more characteristic of SI engine emissions, whereas the heavier alkanes ($>C_{10}$) and aromatic hydrocarbons (such as naphthalene, methyl- and dimethyl- naphthalenes, methyl- and dimethyl-indans) are more characteristic of diesel engine emissions. These differences were the basis for apportionment of gasoline- and diesel-powered vehicle emissions to ambient nonmethane hydrocarbon (NMHC) concentrations in the Boston and Los Angeles (South Coast Air Basin) urban areas. The chemical mass balance receptor model (described below) was applied to ambient samples collected in these areas, along with appropriate fuel, stationary, and area source profiles (Fujita et al., 1997). The average of the sum of NMHC attributed to diesel exhaust, gasoline-vehicle exhaust, liquid gasoline, and gasoline vapor was 73% and 76% for Boston and the South Coast Air Basin (SoCAB), respectively. The average source contributions of diesel exhaust to NMHC concentrations were 22% and 13% for Boston and the SoCAB, respectively. The relative contribution of diesel exhaust will clearly depend on several factors including fleet composition, sampling location (e.g., near a bus station vs. near a highway or other sources), and the contribution from point and area sources. The source apportionment in the Fujita et al. (1997) study indicates that mobile vehicle-related emissions account for the majority of ambient NMHC in the two urban areas studied and the results can likely be extrapolated to other urban areas with similar source compositions.

2.4.2. Ambient Concentrations of Diesel PM

The EPA Office of Air Quality Planning and Standards report on national air pollutant emission trends indicates that annual emissions of diesel PM less than $2.5\ \mu\text{m}$ (PM_{2.5}) nationwide are 5.7% of the total PM_{2.5} inventory (21% excluding natural and fugitive dust sources) (U.S. EPA, 1998b). The inventory includes on-road and off-road sources that have specific local and regional distributions. As a result of inhomogeneous source distributions, ambient diesel PM

concentrations will vary by location. Only a few studies have been conducted to assess diesel PM concentrations in urban and rural areas, local “hotspots,” and the potential for diesel PM episodes. The main approaches used to estimate the contribution of diesel exhaust to ambient PM concentrations are receptor modeling, elemental carbon surrogate calculations, and dispersion modeling. Studies conducted in Europe and Japan were reviewed, but, for the most part, were not included because of questions surrounding the applicability of measurements in locations that use different diesel technology and control measures from the United States.

2.4.2.1. Receptor Modeling Estimates of Diesel PM

Receptor models are used to infer the types and relative contributions of sources impacting a receptor site on the basis of measurements made at the receptor site for the pollutants of interest. As such, receptor models are referred to as “top-down” in contrast to “bottom-up” methods, which use emission inventory data, activity patterns, and dispersion modeling from the source to predict concentrations at a receptor site. Receptor models assume that the mass is conserved between the source and receptor site and that the measured mass of each pollutant is a linear sum of the contribution from each source.

The most commonly used receptor model for quantifying concentrations of diesel PM at a receptor site is the chemical mass balance model (CMB). Input to the CMB model includes PM measurements made at the receptor site as well as measurements made of each of the source types suspected to impact the site. Because of problems involving the elemental similarity between diesel and gasoline emission profiles and their co-emission in time and space, it is necessary to carefully quantify chemical molecular species that provide markers for separation of these sources (Lowenthal et al., 1992). Recent advances in chemical analytical techniques have facilitated the development of sophisticated molecular source profiles, including detailed speciation of organic compounds, which allow the apportionment of PM to gasoline and diesel sources with increased certainty. Older studies that made use of only elemental source profiles have been published and are summarized here, but are subject to more uncertainty.

The CMB model has been used to assess the contribution of diesel PM to total PM mass in areas of California, Denver, Phoenix, and Manhattan (Table 2-13). Diesel PM concentrations reported by Schauer et al. (1996) for data collected in 1982 ranged from 4.4 $\mu\text{g}/\text{m}^3$ in west Los Angeles to 11.6 $\mu\text{g}/\text{m}^3$ in downtown Los Angeles. The average contribution of diesel PM to total PM mass ranged from 13% in Rubidoux to 36% in downtown Los Angeles. It should be noted that this model accounts for primary emissions of diesel PM only; the contribution of secondary aerosol formation (both acid and organic aerosols) is not included. In sites downwind from urban areas, such as Rubidoux in this study, secondary nitrate formation can account for a

Table 2-13. Ambient diesel PM concentrations reported from chemical mass balance modeling

Author	Year of sampling, no. days	Location	Location type	Source profile used	Total PM2.5 (stdev), µg/m ³	Diesel PM2.5 (stdev), µg/m ³
Schauer et al., 1996, Southern California	1982, 60 days (one every sixth day)	West LA Pasadena Rubidoux Downtown LA	Urban Urban Suburban Urban	OC species, EC, elements	24.5 (2.0) 28.2 (1.9) 42.1 (3.3) 32.5 (2.8)	4.4 (0.6) 5.3 (0.7) 5.4 (0.5) 11.6 (1.2)
Chow et al., 1991	Winter, 1989-90, NA	Phoenix, AZ area	Urban	NA	NA	4-22 ^a
California EPA, 1998	1988-92, approx. 150 days	15 Air basins	Rural-urban	EC, OC total, Elements, Major Ions	NA	0.2-3.6 ^a
Federal Highway Admin., 1997b	Spring, 1993, 3 days	Manhattan, NY	Urban bus stop	EC, OC total, elements, major ions	35.8-83.0	13.2-46.7 ^a
NFRAQS, 1998	Winter, 1996-97, 60 days	Welby, CO Brighton, CO	Urban Suburban	OC Species, EC, elements, major ions	16.7 12.4	1.7 1.2

^a PM10.

OC: Organic carbon.

EC: Elemental carbon.

NA: Not available.

Major ions: nitrate, sulfate, chloride and, in some cases, ammonium, sodium, potassium.

substantial fraction of the mass (25% of the fine mass measured in Rubidoux was attributed to secondary nitrate), a portion of which comes from diesel exhaust (Gray and Kuklin, 1996).

A wintertime study conducted in the Phoenix area by Chow et al. (1991) indicated that diesel PM levels on single days can range from 4 $\mu\text{g}/\text{m}^3$ in west and central Phoenix to 14 $\mu\text{g}/\text{m}^3$ in south Scottsdale and 22 $\mu\text{g}/\text{m}^3$ in central Phoenix. This apportionment, like the Schauer et al. (1996) data, reflects direct emissions only. These data relied on source profiles and ambient data collected prior to the introduction of technology to reduce PM emissions from diesel-powered vehicles.

A second CMB study reported ambient diesel PM concentrations for California and used ambient measurements from the San Joaquin Valley (1988-89), South Coast (1986), and San Jose (winters for 1991-92 and 1992-93) (California EPA, 1998a). The incorporation of sampling data from later dates provides information regarding exposures more relevant to current levels. The CMB in the California study (1998a) indicated that on an annual basis, basin-wide levels of direct diesel PM emissions may be as low as 0.2 $\mu\text{g}/\text{m}^3$ in the Great Basin Valleys and as high as 3.6 $\mu\text{g}/\text{m}^3$ in the South Coast basin.

The most recent study reporting diesel PM concentrations is from winter 1996-1997 sampling conducted in the Denver area as part of the Northern Front Range Air Quality Study (NFRAQS), (NRC, 1998). Ambient levels of diesel PM in the urban core site at Welby averaged 1.7 $\mu\text{g}/\text{m}^3$ over a 60-day winter period, and a slightly lower average concentration of 1.2 $\mu\text{g}/\text{m}^3$ was measured at an urban downwind site in Brighton, CO. One of the major findings from this study was a substantial contribution of elemental carbon from gasoline-powered vehicles. At the Welby site, the contribution of diesel and gasoline emissions to elemental carbon measurements was 52% and 42%, respectively. At the Brighton site, the contribution of diesel and gasoline emissions to elemental carbon measurements was 71% and 26%, respectively. The findings from the NFRAQS study are compelling and suggest the need for further investigations of this type that specifically address high-emitting vehicles. Geographical and other site-specific parameters that influence PM concentrations, such as altitude, must be considered when extrapolating the NFRAQS findings to other locations.

Limited data are available to allow a characterization of diesel PM concentrations in "hotspots" such as near heavily traveled roadways, bus stations, train stations, and marinas. One "hotspot" study conducted in Manhattan reported diesel PM concentrations of 13.0 to 46.7 $\mu\text{g}/\text{m}^3$ during a 3-day sampling period in the spring of 1993 (Federal Highway Administration, 1997b). This study attributed, on average, 50% of the PM to diesel exhaust. The diesel PM concentrations resulting from the source apportionment method used in this study require some caution. The CMB model overpredicted PM10 concentrations by an average 30%, suggesting that additional sources of the mass were not accounted for in the model. New advances in organic carbon speciation, as has been noted above, are necessary to most appropriately

1 characterize gasoline and diesel PM sources to ambient PM measurements. The relevance of the
2 Manhattan bus stop exposure for large urban populations provides strong motivation for further
3 studies in the vicinity of such “hotspots.”

4 In summary, recent source apportionment studies (California EPA, 1998a; NRC, 1998)
5 indicate that ambient diesel PM concentrations averaged over 2-12 month periods for
6 urban/suburban areas can range from approximately $1.2 \mu\text{g}/\text{m}^3$ to $3.6 \mu\text{g}/\text{m}^3$, while diesel PM
7 concentrations in more rural/remote areas are generally less than $1.0 \mu\text{g}/\text{m}^3$. In the vicinity of
8 “hotspots,” or for short exposure times under episode-type conditions, diesel PM concentrations
9 are expected to be substantially higher than these levels; however, a thorough and replicated
10 characterization of these situations is not yet available. Two studies nearing completion by the
11 South Coast Air Quality Management District will shed some light on near-highway
12 concentrations of diesel PM (SCAQMD, 1999).

14 **2.4.2.2. *Elemental Carbon Surrogate for Diesel PM***

15 Elemental carbon (EC) is a major component of diesel exhaust, contributing to
16 approximately 60%-80% of diesel particulate mass, depending on engine technology, fuel type,
17 duty cycle, lube oil consumption, and state of engine maintenance (Graboski et al., 1998; Zaebst
18 et al., 1991; Pierson and Brachaczek, 1983; Warner-Selph et al., 1984). In most ambient
19 environments, diesel PM is one of the major contributors to EC, with other potential sources
20 including spark-engine exhaust; combustion of coal, oil, or wood; charbroiling; cigarette smoke;
21 and road dust. Gasoline combustion was recently found to be an important source of elemental
22 carbon in Denver (NRC, 1998).

23 Because of the large portion of EC in diesel PM, and the fact that diesel exhaust is one of
24 the major contributors to EC in most ambient environments, diesel PM concentrations can be
25 bounded using EC measurements. Source apportionment (NRC, 1998) indicates that diesel
26 exhaust comprises from 52% to 71% of the elemental carbon concentrations in ambient PM in the
27 Denver area for the winter of 1996-97. If we assume that gasoline and diesel exhaust
28 contributions to EC measured in Denver will be similar to other areas, a plausible estimate of
29 diesel particulate concentrations can be calculated by multiplying a measured EC concentration by
30 64% and dividing by the fraction of diesel PM mass accounted for by EC (note: a middle-of-the-
31 range value of 70% was chosen for illustrative purposes), e.g., diesel PM concentration = $[(\text{EC} * 0.64)/0.7]$. This estimate uses an average of the diesel contributions to EC observed in Denver
32 with contributions from other, potentially site-specific sources of EC subtracted (e.g., wood
33 smoke). An upper-bound estimate of diesel PM from EC measurements would attribute all
34 ambient EC to diesel exhaust, e.g., diesel PM concentration = $\text{EC}/0.7$, which may be applicable to
35 some occupational exposures.
36

The surrogate diesel PM calculation is a useful approach for estimating diesel PM in the absence of a more sophisticated receptor modeling analysis for locations where fine PM elemental carbon concentrations are available. Table 2-14 provides diesel PM concentrations that were calculated using the EC surrogate ratiometric approach. Under an EPA Research Grant with the Northeastern States for Coordinated Air Use Management (NESCAUM), PM_{2.5} samples were collected in Boston (Kenmore Square), MA, Rochester, NY, Reading, MA, Quabbin Reservoir, MA, and Brockport, NY (Salmon et al., 1997). Samples were collected every sixth day for one year (1995). Using the EC surrogate calculation described above, diesel PM concentrations are estimated to range from 0.3 µg/m³ in Brockport, NY to 1.1 µg/m³ in Boston.

The Interagency Monitoring of Protected Visual Environments (IMPROVE) project of the National Park Service operates an extensive aerosol monitoring network in mainly rural or remote areas of the country (National Parks, National Monuments, Wilderness Areas, National Wildlife Refuges, and National Seashores). PM_{2.5} samples, collected twice weekly for 24-hour duration, at 43 sites (some co-located in the same rural park area) were analyzed for a suite of chemical constituents, including elemental carbon. The IMPROVE data in Table 2-14 represent average values for the period from March 1992 through February 1995 (Sisler, 1996).

Table 2-14. Diesel PM 2.5 concentrations in urban and rural locations using EC surrogate^a for NESCAUM (1995) and IMPROVE (1992-1995) network sites

Area	Annual average PM _{2.5} µg/m ³	Diesel PM _{2.5} µg/m ³
Urban areas		
Boston, MA ^b	16.2	1.1
Rochester, NY ^b	14.9	0.5
Washington, DC ^c	19.2	1.6
Nonurban areas		
Quabbin, MA ^b	12.4	0.4
Reading, MA ^b	14.6	0.6
Brockport, NY ^b	12.8	0.3
IMPROVE sites	1.8-12.1	0.1-0.8

^a Assumes 64% of EC mass is from diesel exhaust and 70% of diesel PM is elemental carbon.

^b NESCAUM sites.

^c IMPROVE sites.

The estimated diesel PM concentrations for rural/remote areas from the IMPROVE network ranged from 0.1 µg/m³ for Denali National Park, AK, to 0.8 µg/m³ for the Lake Tahoe, CA, area (which includes on-road and off-road diesel emissions). The diesel PM concentrations

1 in rural areas of the northeastern States are similar to those calculated for rural areas in other
2 parts of the country, with all values less than $1.0 \mu\text{g}/\text{m}^3$. Among the urban areas included in the
3 NESCAUM and IMPROVE networks, Washington, DC, had the highest calculated diesel PM
4 concentration of $1.6 \mu\text{g}/\text{m}^3$. The annual average value for Washington, DC, is quite similar to the
5 wintertime diesel PM concentrations reported for Denver (NRC, 1998). Seasonally averaged data
6 for the Washington, DC, site indicates that EC concentrations, and by extension, diesel PM
7 concentrations at this site peak in the autumn and winter (1.9 and $1.8 \mu\text{g}/\text{m}^3$ diesel PM,
8 respectively).

9 Recently, EC measurements were reported for enclosed vehicles driving on Los Angeles
10 roadways (California EPA, 1998b). Applying the ratiometric approach for diesel PM
11 determinations from EC measurements, diesel PM concentrations in the vehicle ranged from
12 approximately $2.8 \mu\text{g}/\text{m}^3$ to $36.6 \mu\text{g}/\text{m}^3$ depending on the type of vehicle being followed (higher
13 concentrations were observed when the vehicle followed HD diesels). The California Air
14 Resources Board also collected EC near the Long Beach Freeway for 4 days in May 1993 and 3
15 days in December 1993 (California EPA, 1998a). Using emission estimates from their
16 EMFAC7G model, and elemental/organic carbon composition profiles for diesel and gasoline
17 exhaust, tire wear, and road dust, the California Air Resources Board estimated the contribution
18 of the freeway to diesel PM concentrations. For the 2 days of sampling in December 1993, diesel
19 exhaust from vehicles on the nearby freeway were estimated to contribute from $0.7 \mu\text{g}/\text{m}^3$ to 4.0
20 $\mu\text{g}/\text{m}^3$ excess diesel PM above background concentrations, with a maximum of $7.5 \mu\text{g}/\text{m}^3$.

21 In two additional studies, EC concentrations were measured in Glendora, CA, during a
22 carbonaceous aerosol intercomparison study (Cadle and Mulawa, 1990; Hansen and Novakov,
23 1990). EC concentrations ranged from $5.0 \mu\text{g}/\text{m}^3$ to $6.4 \mu\text{g}/\text{m}^3$, corresponding to diesel PM
24 concentrations of $4.6 \mu\text{g}/\text{m}^3$ to $5.9 \mu\text{g}/\text{m}^3$ using the ratiometric approach described above. One
25 technique used during the study reported EC concentrations in 1-minute intervals, revealing the
26 impact from diesel vehicles 50 meters from the study site. The diesel vehicles were estimated to
27 contribute up to $5 \mu\text{g}/\text{m}^3$ EC above the background concentration.

28 In a study designed to investigate relationships between diesel exhaust exposure and
29 respiratory health of children in the Netherlands, EC measurements were collected in 23 schools
30 located from 47 to 377 meters from a freeway and in 8 schools located at a distance greater than
31 400 meters from a freeway (Brunekreef, 1999). EC concentrations in schools near freeways
32 ranged from 1.1 to $6.3 \mu\text{g}/\text{m}^3$, with a mean of $3.4 \mu\text{g}/\text{m}^3$, and EC concentrations in schools more
33 than 400 meters from freeways ranged from 0.8 to $2.1 \mu\text{g}/\text{m}^3$ with a mean of $1.4 \mu\text{g}/\text{m}^3$. Using
34 the EC surrogate calculation for diesel PM described above, the estimated average diesel PM
35 concentration in the schools near a freeway is $3.1 \mu\text{g}/\text{m}^3$ and the estimated average diesel PM
36 concentration in schools located more than 400 meters from a freeway is $1.3 \mu\text{g}/\text{m}^3$. Total PM_{2.5}

1 mass inside the schools averaged 23.0 $\mu\text{g}/\text{m}^3$ while PM_{2.5} outside was only slightly higher (24.8
2 $\mu\text{g}/\text{m}^3$), suggesting extensive intrusion of outdoor air into the school environment.

3 4 **2.4.2.3. Dispersion Modeling Results**

5 Dispersion models estimate ambient levels of PM at a receptor site on the basis of
6 emission factors for the relevant sources and the investigator's ability to model the advection,
7 mixing, deposition, and chemical transformation of compounds from the source to the receptor
8 site. Cass and Gray (1995), Gray and Cass (1998), and Kleeman and Cass (1998) have applied
9 dispersion models to the South Coast Air Basin to estimate diesel PM concentrations. The
10 models used by these investigators applied emission factors from 1982 and consequently are
11 representative of concentrations prior to the implementation of diesel PM emission controls. In
12 addition to offering another approach for estimating ambient diesel PM concentrations, the
13 dispersion models summarized here provide the ability to distinguish on-highway from off-
14 highway diesel source contributions and have presented an approach for quantifying the
15 concentrations of secondary aerosols from diesel exhaust.

16 Cass and Gray (1995) used a Lagrangian particle-in-cell model to estimate the source
17 contributions to atmospheric fine carbon particle concentrations in the Los Angeles area,
18 including diesel emission factors from on-highway and off-highway sources. Their dispersion
19 model indicates that for 1982, the annual average ambient concentrations of diesel PM ranged
20 from 1.9 $\mu\text{g}/\text{m}^3$ in Azusa, CA, to 5.6 $\mu\text{g}/\text{m}^3$ in downtown Los Angeles (Table 2-15). The
21 contribution of on-highway sources to diesel PM ranged from 63.3% in downtown Los Angeles
22 to 89% in West Los Angeles. Of the on-highway diesel contribution, the model predicted that for
23 southern California, HD trucks comprised the majority (85%) of the diesel PM inventory and
24 overall they contributed 66% of the diesel PM in the ambient air. Off-road sources of diesel
25 exhaust include pumping stations, construction sites, shipping docks, railroad yards, and heavy
26 equipment repair facilities. Cass and Gray (1995) also report that wintertime peaks in diesel PM
27 concentrations can reach 10 $\mu\text{g}/\text{m}^3$.

28 Kleeman and Cass (1998) developed a Lagrangian model that examines the size and
29 chemical evolution of aerosols including gas-to-particle conversion processes during transport.
30 This model was applied to one-well characterized episode in Claremont County, CA, on August

Table 2-15. Modeled diesel PM_{2.1} for South Coast Air Basin in 1982^a

Location	On-highway diesel PM, $\mu\text{g}/\text{m}^3$	Total diesel PM, $\mu\text{g}/\text{m}^3$	% On-highway
Azusa	1.4	1.9	75
Pasadena	2.0	2.5	78
Anaheim	2.7	3.5	78
Long Beach	3.5	4.6	76
Downtown Los Angeles	3.5	5.6	63
Lennox	3.8	4.7	81
West Los Angeles	3.8	4.3	89

^aAdapted from Cass and Gray (1995), modeling results of Gray (1986).

27-28, 1987. The model provided reasonable predictions of PM₁₀ (overpredicting PM₁₀ 13%), elemental and organic carbon, and adequately reconstructed the size distribution of the aerosols. The model indicated that on August 27-28, 1987, the PM_{2.5} concentration was 76.7 $\mu\text{g}/\text{m}^3$, 13.2% of which (10.1 $\mu\text{g}/\text{m}^3$) was attributable to diesel engine emissions. This estimate includes secondary aerosol formation for sulfate, ammonium, nitrate, and organic compounds, which accounted for 4.9 $\mu\text{g}/\text{m}^3$ of the total estimated diesel PM mass. The secondary organic aerosol was estimated to be 1.1 $\mu\text{g}/\text{m}^3$, or 31% of the total secondary aerosol mass, with the remainder composed of nitrate, ammonium, and sulfate aerosols.

Dispersion modeling is also being conducted by EPA to estimate county-specific concentrations of, and exposures to, several toxic species, including diesel PM. Results from this model are expected in 2000.

2.4.3. Exposures to Diesel PM

Up to this point, the information on diesel PM has focused on estimates of concentrations in outdoor environments. Ultimately, it is personal exposure that determines health impacts. Personal exposures can be measured using surrogate chemical species such as EC, or exposures can be modeled. Results of both exposure assessment methods are discussed below.

Occupational exposures to diesel PM were reported for long-distance truck drivers, local drivers, mechanics, and dockworkers by Zaebst et al. (1991), and other occupational exposures are summarized by Watts (1995) and Birch and Cary (1996). Two modeling efforts have been developed to determine diesel PM exposures in the general population: the Hazardous Air

Pollutant Exposure Model-Mobile Sources version 3 (HAPEM-MS3) and the California Population Indoor Exposure Model (CPIEM).

2.4.3.1. Exposure Measurements

Occupational exposures to diesel PM were estimated by Zaebst et al. (1991), who reported EC measurements from personal samplers worn by road drivers, local drivers, dockworkers, and mechanics for 8-hour shifts at each of six large hub truck terminals. Residential background and highway background samples at fixed sites were also collected. Zaebst et al. (1991) reported warm- and cold-weather EC concentrations in residential background and highway background environments, which ranged from 0.9 $\mu\text{g}/\text{m}^3$ to 4.9 $\mu\text{g}/\text{m}^3$. Elemental carbon exposures for road and local truckers ranged from 2.0 $\mu\text{g}/\text{m}^3$ to 7.0 $\mu\text{g}/\text{m}^3$, while exposure levels for mechanics and dockworkers were reported between 4.8 $\mu\text{g}/\text{m}^3$ and 28.0 $\mu\text{g}/\text{m}^3$.

The geometric mean of the EC concentrations reported by Zaebst et al. (1991) was adjusted for the potential contribution of other EC sources using the ratiometric approach described above. The estimated diesel PM exposures calculated range from 3.5 $\mu\text{g}/\text{m}^3$ and 3.7 $\mu\text{g}/\text{m}^3$ for road and local drivers, respectively, to 12.6 $\mu\text{g}/\text{m}^3$ for mechanics (Table 2-16). Important variables in this calculation include the potential contribution of 2-stroke diesel engines (which generate PM with lower EC concentrations than 4-stroke diesel engines) and the contribution of other EC sources such as cigarette smoke, wood smoke, or gasoline combustion above the level accounted for. The exposure levels for road and local drivers to diesel PM estimated from the Zaebst et al. (1991) study are a factor of 2 to 3 higher than recent ambient PM levels reported for Denver, which is reasonable given that drivers are likely to be in closer proximity to traffic than at either of the two Denver fixed sites.

Additional occupational exposures to EC have been reported for miners, fire engine operators in engine houses, automotive repair shops dedicated to diesel vehicles, service bay workers in a public transit system, and aircraft ground crews (Birch and Cary, 1996; Watts, 1995). Diesel PM exposures were calculated from the EC exposures using an upper-bound estimate (e.g., EC concentration = diesel PM/0.7) because the workers were generally in confined spaces in which diesel exhaust was the dominant source of EC. If this upper-bound estimate is applied, the calculated occupational exposures to diesel PM range from 10 to 21 $\mu\text{g}/\text{m}^3$ for an aircraft ground crew, and up to 43 $\mu\text{g}/\text{m}^3$, 113 $\mu\text{g}/\text{m}^3$, and 140 $\mu\text{g}/\text{m}^3$ for bus public transit areas, firefighters in the station house, and bus transit service bay personnel, respectively. In additional occupational settings, breathing zone concentrations of EC have been reported by Birch and Cary

Table 2-16. Diesel PM_{1.0} exposures reported by Zaebst et al. (1991) and calculated using the EC ratiometric approach^a

Location/job type	Number of samples	Geom. mean diesel PM (stdev) $\mu\text{g}/\text{m}^3$	Calculated diesel PM ^a , $\mu\text{g}/\text{m}^3$
Residential background	23	1.1 (2.0)	1.0
Highway background	21	2.5 (2.4)	2.3
Road drivers	72	3.8 (2.3)	3.5
Local drivers	56	4.0 (2.0)	3.7
Dockworkers	75	12.1 (3.7)	11.1
Mechanics	80	13.8 (3.6)	12.6

^a Diesel PM=(EC*0.64)/0.7.

(1996) and the estimated maximum diesel PM concentrations from these measurements suggest levels of $24 \mu\text{g}/\text{m}^3$ for a beverage distributor warehouse, $100 \mu\text{g}/\text{m}^3$ for diesel automotive repair crews, $286 \mu\text{g}/\text{m}^3$ for a front end loader operator in a confined space of a timber processing plant, and $976 \mu\text{g}/\text{m}^3$ for a firehouse bay area.

Watts (1995) reports diesel PM sampling conducted in mines during significant diesel activity, which does not represent personal exposures, but is a snapshot of short periods of elevated concentration that comprise a portion of a worker's daily exposure. The levels of diesel PM in four mines ranged from $850 \mu\text{g}/\text{m}^3$ to $3260 \mu\text{g}/\text{m}^3$. In a study of four railroads, Woskie et al. (1988) reported concentrations of respirable dust (corrected for cigarette particulate) that ranged from $17 \mu\text{g}/\text{m}^3$ for clerks to $130 \mu\text{g}/\text{m}^3$, $134 \mu\text{g}/\text{m}^3$, and $191 \mu\text{g}/\text{m}^3$ for supervisors, electricians, and hostlers, respectively. Although these exposures may have included nondiesel PM, the majority of the respirable PM is believed to have originated from the locomotive emissions.

2.4.3.2. Modeling Exposures to Diesel PM

Modeled estimates of individual exposures to diesel PM must integrate exposure in the various indoor and outdoor environments in which different individuals are active. Consequently, the demographic distribution, time-activity patterns, and diesel PM concentrations in the various environments, including job-related exposures, must all be taken into account.

2.4.3.2.1. The Hazardous Air Pollutant Exposure Model for Mobile Sources, version 3. The HAPEM-MS3 model is based on the carbon monoxide (CO) probabilistic NAAQS exposure model (CO pNEM), which is used to estimate the frequency distribution of population exposure to CO and the resulting carboxyhemoglobin levels (Law et al., 1997). The HAPEM model simulates the CO exposure scenario of individuals in 22 demographic groups for 37 microenvironments. CO concentrations are based on ambient measurements made in 1990 and are related to exposures of individuals in a 10 km radius around the sampling site. Diesel PM (DPM) exposures are calculated as in Equation 2-4, using a ratiometric approach to CO.

$$DPM_{\mu\text{g}/\text{m}^3} = (CO_{\mu\text{g}/\text{m}^3} / CO_{\text{g}/\text{mi}}) \times DPM_{\text{g}/\text{mi}} \quad (2-4)$$

Input to the model includes CO monitoring data for 1990, time-activity data collected in Denver, CO, Washington DC, and Cincinnati, OH, from 1982 to 1985, microenvironmental data, and 1990 census population data. Motor vehicle diesel PM and CO emission rates reported by EPA (1999b) are used to calculate mobile-source diesel PM exposures. While gasoline vehicles emit the large majority of CO, gasoline and diesel highway vehicles travel on the same roadways, albeit with different spatial and temporal patterns. Nevertheless, the assumption can be made that the highway fleet (gasoline+diesel) emissions ratio of CO to diesel PM can be used as an adjustment factor to convert known or estimated CO personal exposure to diesel PM exposure estimates.

This modeling approach was first used to estimate population average exposures among 22 demographic groups for 9 urban areas (U.S. EPA, 1999b). The exposures were calculated based on air districts, which were defined as the population within the 10 km radius of the CO monitor. Employing average CO exposures in this approach may underestimate by approximately 30% the exposures experienced by the 98th percentile population (Law et al., 1997). In order to characterize exposures in these highly exposed populations, Brodowicz (1999) used CO concentrations relevant to the most highly exposed populations to determine diesel PM exposures for different demographic groups within this population. Results for both the annual average diesel PM exposures and exposures in the most highly exposed demographic groups are given in Table 2-17.

The annual average diesel PM exposures ranged from 0.6 $\mu\text{g}/\text{m}^3$ in Spokane, WA, to 1.7 $\mu\text{g}/\text{m}^3$ in New York (Table 2-17). The highest diesel PM exposures ranged from 0.9 $\mu\text{g}/\text{m}^3$ for outdoor workers in St. Louis to 4.1 $\mu\text{g}/\text{m}^3$ for outdoor children in New York (Table 2-17). The highest exposed demographic groups were those who spend a large portion of their time outdoors. Overall, the highest exposed individuals experienced diesel PM levels that were on

Table 2-17. Annual average diesel PM exposures for 1990 in the general population and among the highest exposed demographic groups in nine urban areas (on-road sources only)

Urban area	Population average exposure, $\mu\text{g}/\text{m}^3$	Highest diesel PM exposure, $\mu\text{g}/\text{m}^3$ (demographic group experiencing this exposure)
Chicago, IL	0.8	1.3 (outdoor workers)
Denver, CO	0.8	1.3 (outdoor workers)
Houston, TX	0.6	0.9 (outdoor workers)
Minneapolis, MN	1.0	1.6 (outdoor workers)
New York, NY	1.7	4.1 (outdoor children)
Philadelphia, PA	0.7	1.3 (outdoor children)
Phoenix, AZ	1.4	2.6 (nonworking men 18-44)
Spokane, WA	1.3	2.0 (outdoor workers)
St. Louis, MO	0.6	0.9 (outdoor workers)

average 1.7 times higher than the population average. Exposures to diesel PM in rural areas nationwide were estimated by HAPEM-MS3 to be $0.5 \mu\text{g}/\text{m}^3$. It is important to note that these exposure estimates are lower than the total exposure to diesel PM because they reflect only diesel PM from on-road sources (U.S. EPA, 1998b).

Diesel PM exposure projections were calculated using the HAPEM model for 1996, 2007, and 2020 with a base case and a case assuming increased penetration of diesel engines in the LD truck fleet. The base case uses baseline fuels and emission rates, assuming the implementation of a National Low-Emission Vehicle (NLEV) program. The increased dieselization case uses baseline emission factors with Tier 2 standards and an assumed increase in LD diesel truck implementation equivalent to 50% of the LD truck sales beginning in model year 2004 (which is more aggressive than the likely increase in diesel engine market share).

Predicted diesel PM exposures for 2007 and 2020 decrease from 1996 levels by an average 55% and range from a low of $0.3 \mu\text{g}/\text{m}^3$ in St. Louis to a high of $0.6 \mu\text{g}/\text{m}^3$ in Phoenix, for both 2007 and 2020 (Table 2-18). The predicted decreases are a result of fleet turnover and the full implementation of Federal regulations that are currently in place. If the modeled increase

Table 2-18. Projected annual average diesel PM exposures from all on-road vehicles

Area	Diesel PM exposure by calendar year, $\mu\text{g}/\text{m}^3$		
	1996	2007	2020
Chicago, IL	0.6	0.3	0.3
Denver, CO	0.7	0.4	0.4
Houston, TX	0.8	0.3	0.3
Minneapolis, MN	0.9	0.4	0.4
New York, NY	1.1	0.5	0.5
Philadelphia, PA	0.6	0.3	0.2
Phoenix, AZ	1.2	0.6	0.6
Spokane, WA	1.0	0.5	0.5
St. Louis, MO	0.5	0.3	0.2

in diesels in the LD truck fleet occurs, projected diesel PM exposures are expected to increase 38% on average over 1996 exposures. If diesel engines reached 50% of the light duty truck sales in 2010, instead of 2004, the increase in diesel PM exposure would be about 30%.

2.4.3.2.2. The California Population Indoor Exposure Model. The California Population Indoor Exposure Model (CPIEM), developed under contract to the California Air Resources Board, estimates Californians' exposure to diesel PM using distributions of input data and a Monte Carlo approach (California EPA, 1998a). This model uses population-weighted outdoor diesel PM concentrations in a mass-balance model to estimate diesel PM concentrations in four indoor environments: residences, office buildings, schools, and stores/retail buildings. The model takes into account air exchange rates, penetration factors, and a net loss factor for deposition/removal. In four additional environments (industrial plants, restaurants/lounges, other indoor places, and enclosed vehicles), assumptions were made about the similarity of each of these spaces to environments for which diesel PM exposures had been calculated. Industrial plants and enclosed vehicles were assumed to have diesel PM exposures similar to those in the outdoor environment, restaurant/lounges were assumed to have diesel PM concentrations similar to stores, and other indoor places were assumed to have diesel PM concentrations similar to offices. The estimated diesel PM concentrations in the indoor and outdoor environments range from $1.6 \mu\text{g}/\text{m}^3$ to $3.0 \mu\text{g}/\text{m}^3$ (Table 2-19).

Table 2-19. Modeled and estimated concentrations of diesel PM in microenvironments (California EPA, 1998a)

Environment	Estimated mean diesel PM (stdev), $\mu\text{g}/\text{m}^3$
Residences	1.9 (0.9)
Offices	1.6 (0.7)
Schools	1.9 (0.8)
Stores/public/retail bldgs	2.1 (0.9)
Outdoor places	3.0 (1.1)
Industrial plants ^a	3.0 (1.1)
Restaurants/lounges ^a	2.1 (0.9)
Other indoor places ^a	1.6 (0.7)
Enclosed vehicles ^a	3.0 (1.1)

^aConcentrations assumed based on similarity with modeled environments.

The diesel PM concentrations reported in Table 2-19 were used as input to the CPIEM model, and time-activity patterns for children and adults were used to estimate total indoor and total air exposures to diesel PM. Overall, total indoor exposures were estimated at $2.0 \pm 0.7 \mu\text{g}/\text{m}^3$ and total air exposures (indoor and outdoor exposures) were $2.1 \pm 0.7 \mu\text{g}/\text{m}^3$ (Table 2-20). The South Coast Air Basin and the San Francisco Bay Area were also modeled using CPIEM, where total air exposures to diesel PM were estimated to be $2.5 \pm 0.9 \mu\text{g}/\text{m}^3$ and $1.7 \pm 0.9 \mu\text{g}/\text{m}^3$, respectively.

Exposure estimates were also made by California EPA (1998a) for 1995, 2000, and 2010 using a ratiometric approach to 1990 exposures. Total air exposures reported for 1995 and projected for 2000 and 2010 were $1.5 \mu\text{g}/\text{m}^3$, $1.3 \mu\text{g}/\text{m}^3$, and $1.2 \mu\text{g}/\text{m}^3$, respectively.

2.4.4. Ambient Diesel PM Summary

It appears from the limited number of studies available that annually averaged diesel PM concentrations at fixed sites in urban and suburban areas in the 1980s ranged from approximately $4.4 \mu\text{g}/\text{m}^3$ to $11.6 \mu\text{g}/\text{m}^3$. CMB and dispersion modeling indicate that diesel PM concentrations on some winter days may reach $22 \mu\text{g}/\text{m}^3$ and on episode days concentrations of $10 \mu\text{g}/\text{m}^3$ are possible. CMB modeling results, which include emissions and measurements from 1990 and

Table 2-20. Estimated indoor air and total air exposures to diesel PM in California in 1990

Exposed population	Total indoor exposure (stdev), $\mu\text{g}/\text{m}^3$	Total air exposure, (stdev), $\mu\text{g}/\text{m}^3$
All Californians	2.0 (0.7)	2.1 (0.8)
South Coast Air Basin	2.4 (0.9)	2.5 (0.9)
San Francisco Bay Area	1.7 (0.9)	1.7 (0.9)

later, indicate that diesel PM concentrations in “hotspots” may reach $46.7 \mu\text{g}/\text{m}^3$; diesel PM concentrations at fixed sites in urban and suburban areas range from approximately $1.2 \mu\text{g}/\text{m}^3$ to $3.6 \mu\text{g}/\text{m}^3$. Annual average diesel PM concentrations in rural and remote areas of the country are less than $1.0 \mu\text{g}/\text{m}^3$.

Measurements of the diesel PM surrogate, EC, in rural and urban environments indicate concentrations similar to those reported by CMB methods, with diesel PM concentrations less than $1.0 \mu\text{g}/\text{m}^3$ in rural areas and concentrations from approximately $0.5 \mu\text{g}/\text{m}^3$ to $5.9 \mu\text{g}/\text{m}^3$ in urban areas. The EC surrogate approach also provides some estimates of diesel PM in microenvironments such as in-vehicle concentrations ($2.8\text{--}36.6 \mu\text{g}/\text{m}^3$), near roadways with diesel traffic ($0.7\text{--}7.5 \mu\text{g}/\text{m}^3$ higher than background), and in schools ($0.9\text{--}5.5 \mu\text{g}/\text{m}^3$). Measurements of EC in occupational environments indicate that diesel PM exposures range from approximately $3.5 \mu\text{g}/\text{m}^3$ for long distance diesel truck drivers to $140 \mu\text{g}/\text{m}^3$ for bus transit service bay personnel.

It is noteworthy that the annually averaged concentrations and exposures will mask potentially important excursions experienced during episodic conditions, and/or seasonal elevations that may have important associated health risks. Individuals for whom exposures are equal to, or may greatly exceed, the annual average ambient diesel PM levels reported here may include those who spend a significant portion of their day on or near roadways, such as sales representatives, delivery personnel, construction workers, and individuals living in the vicinity of “hotspots” (near highway, bus depot, or other transit facility).

The HAPEM-MS3 exposure model, which assesses exposures from on-road diesel emissions only, indicates that on an annual basis the urban population is exposed to levels of diesel PM from $0.6 \mu\text{g}/\text{m}^3$ to $1.7 \mu\text{g}/\text{m}^3$. Diesel PM exposures for the most highly exposed individuals in urban areas are estimated by HAPEM-MS3 to range from $0.9 \mu\text{g}/\text{m}^3$ to $4.1 \mu\text{g}/\text{m}^3$, with individuals spending a large amount of time outside comprising the highest exposure group. The

California EPA (1998a) exposure model, which assesses diesel PM exposures from on- and off-road sources, reports diesel PM exposures for Californians ranging from 1.7 $\mu\text{g}/\text{m}^3$ to 2.5 $\mu\text{g}/\text{m}^3$. Projected diesel PM exposure levels are expected to decrease by 2007 in the absence of an increase in LD diesel truck implementation.

2.5. SUMMARY

Dieselization of the trucking industry first occurred in the 1930s, and reached 40%-50% of the market for Class 7 and 8 trucks (based on sales data) by early 1960. By the late 1980s, more than 95% of heavy trucks used diesel engines. Dieselization of locomotives began at the end of the Second World War and was completed rapidly, probably by the early 1950s. Technology innovations that impact emissions have occurred in the years since 1960, in particular the advent of turbocharging with charge air cooling, and DI engines. These advances have tended to lower emissions, but until the late 1980s engines were optimized for performance rather than emissions, so the effect was small. Overall, it is expected that engines in the 1950 to 1980s time frame would have PM emissions similar to those of the mid-1980 engines that were not yet controlled for particulates.

The proportion of 2-stroke engines in the in-use truck fleet was in all likelihood 20%-25% for most of the time from 1960 to 1985. Only in the late 1980s did 2-stroke engines begin to decline. Overall, regulated emissions changes due to changing proportions of 2- and 4-stroke engines in the in-use fleet during the years 1949-1975 do not appear to be significant for HD truck and bus engines. No significant difference in PM mass emissions between 2- and 4-stroke vehicles are evident; however, 2-stroke engines emitted PM with a higher organic and higher amounts of VOCs than did 4-stroke engines.

Regulated emissions of CO, HC, and PM have declined significantly for on-road trucks since the mid-1970s. PM emissions appear to have decreased by a factor of 6 while emissions of NO_x have remained approximately constant. Emissions trends for earlier years are unknown; however, given that there were no emissions regulations in effect until the early 1970s it is likely that emissions were fairly constant during the 1960s. Little change in locomotive emissions from the early 1970s to the 1990s is evident. It is likely that this trend can also be extrapolated back to the mid-1950s.

Data on nonregulated emissions and particle size were reviewed. It is apparent that the soluble organic fraction of particulate, as well as the solid portion, have declined during the past two decades. EC content comprises the largest fraction of diesel PM and so has declined. There is also evidence for a decrease in the percentage of organics adsorbed on the particulates over time. Emissions of PAHs and nitro-PAHs appear to have declined in parallel with emissions of

total PM and SOF. There is no evidence to suggest that toxicologically significant organic components of DE (e.g., PAHs and nitroaromatics) have changed out of proportion to the change in organic mass.

Particle size measurements suggest that the size distribution for current emissions may be shifted more toward slightly higher number concentrations of nuclei-mode particles. However, methodologies for assessing nuclei particles are in a very early stage of technical development and no conclusions can be made at the current time.

The dilution of exhaust under roadway conditions is not well simulated by dynamometer dilution tunnel tests (dilution ratios of approximately 1000 in the ambient environment, compared to 10-fold dilution in laboratory tests). This discrepancy may lead to particle size distribution and gas-particle phase distributions of semivolatile compounds under conditions slightly different from those predicted from laboratory data. Diesel engines emit several toxicologically important compounds, including nitroarenes and other PAH compounds. The chemical and physical changes of diesel exhaust in the atmosphere have been extensively explored, but knowledge concerning the products of these chemical transformations is still limited and is challenging to predict from laboratory tests. In general, diesel exhaust components will become more oxidized in the atmosphere, making them more polar and therefore more water-soluble. Secondary aerosols from diesel exhaust may be removed at rates different from their precursor compounds, and may exhibit different biological reactivities.

Diesel PM concentrations reported from chemical mass balance studies in the 1980s suggest that annually averaged concentrations ranged from approximately $4.4 \mu\text{g}/\text{m}^3$ to $11.6 \mu\text{g}/\text{m}^3$. More recent analysis suggests that annually averaged ambient concentrations of diesel PM range from $0.2 \mu\text{g}/\text{m}^3$ to $3.6 \mu\text{g}/\text{m}^3$, with levels below $1.0 \mu\text{g}/\text{m}^3$ for the more rural/remote areas. Chemical mass balance modeling and dispersion analysis suggest that in urban hot spots and during episodic conditions, diesel PM concentrations may be as high as $10\text{--}47 \mu\text{g}/\text{m}^3$. Exposure modeling has indicated that individuals from the general population in urban areas may be exposed to $0.6\text{--}1.7 \mu\text{g}/\text{m}^3$ diesel PM, while those individuals who spend a large amount of their time out of doors may have exposures ranging up to $4.1 \mu\text{g}/\text{m}^3$. Diesel PM exposures in some occupational environments can exceed these levels by 2-3 orders of magnitude.

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